VOL. XXI. MARCH, 1899. NO. 3.

AMERICAN CHEMICAL JOURNAL

Contributions from the Sheffield Laboratory of Yale University.

LXVIII.—ON THE REARRANGEMENT OF IMIDO-ESTERS.

BY H. L. WHEELER AND T. B. JOHNSON.

The fact that the silver salts of the amides give imido-esters with alkyl halides was observed simultaneously, in the year 1890, by Tafel and Enoch[1] and by Comstock.[2] As we had occasion to prepare ethyl phenylimidoformate, $HC\langle^{NC_6H_5}_{OC_2H_5}$, by their method, and, wishing to avoid the slow process of warming silver formanilide suspended in ether with ethyl iodide for several days, we heated a portion of the silver salt to 100° in a closed tube with an excess of ethyl iodide. An oil was thus obtained which did not contain a trace of the expected imido-ester. The entire reaction-product was *N*-ethyl-formanilide, $H-C(=O)-N(C_6H_5)C_2H_5$.

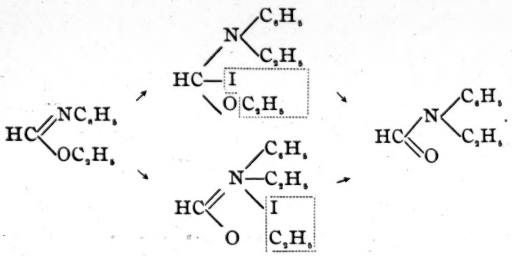
In order to assure ourselves that our material was not at fault, we boiled another portion of the same sample of silver salt, in an open vessel, with an ether solution of ethyl iodide and got an excellent yield of the sought-for, isomeric, imido-ester.

1 Ber. d. chem. Ges., **23**, 103 and 1550.
2 *Ibid.*, **23**, 2274 and R. 659; also This JOURNAL, **13**, 514.

This "tautomeric" reaction of the silver salt with ethyl iodide is remarkable since the difference of conditions in the two cases cited is so small—a difference of temperature less than 65° and only slight increase in pressure in the case of the reaction in the closed tube.[1]

Another portion of the same salt was heated again in a closed tube to 100°, as in the previous experiment, except that in this case a little less than the calculated amount of ethyl iodide was used, when little or no imido-ester was obtained.

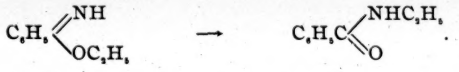
These facts suggested that in the case of the reactions in the closed tube we have not a single reaction but a set of reactions. The first and intermediate product, the imido-ester, under the conditions of the experiment, reacts further with the ethyl iodide to give *N*-ethylformanilide. This must take place by addition in either of the following two ways :



That is, ethyl iodide is either added to the carbon and nitrogen that are doubly linked together, or entirely to the nitrogen, and then separates again in another manner as indicated by the dotted lines.

[1] These striking results show that the method of preparation of a compound proves nothing in regard to its structure and that arguments concerning structure, based solely on the compounds formed in a reaction, have no weight. In the sodium salts of the amides the metal is universally represented as attached to nitrogen simply because these salts give nitrogen alkyl compounds with alkyl halides. That the metal is attached to nitrogen in these compounds is improbable. The above reactions show that slight changes in conditions may produce opposite results, and the difference in conditions when alkyl halides act on sodium salts on the one hand and on silver salts on the other, is certainly great—greater at least than is necessary to produce the opposite results in the case of the same material, *i. e.*, the silver salts.

That this is the course of the reaction is shown by the fact that benzimidoethylester, prepared by Pinner's method from benzonitril, when heated with ethyl iodide at 100°, gives practically nothing but ethylbenzamide :



The reaction taking place as shown above has the effect of simply transferring the ethyl from its union with oxygen to the nitrogen.

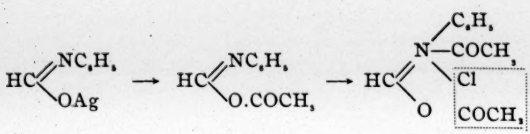
The tautomeric reaction in these cases, as in others, is undoubtedly nothing but a reaction by addition.

The above cases are the first that have been observed where a silver salt of an acyclic amide, anilide, or imido-ester give nitrogen derivatives with alkyl iodides.[1] The behavior of the silver salts and imido-esters with alkyl halides under pressure and at a somewhat elevated temperature is analogous to their behavior with acyl chlorides in the cold. It was shown in previous papers,[2] on the compounds in question that the silver and mercury salts of the anilides, and the corresponding imido-esters give the same diacylanilides, and that nitrogen-substituted derivatives resulted in each case.

The above action of ethyl iodide on silver formanilide explains the behavior of acyl chlorides with the silver salts—a "tautomeric" reaction when compared with our previous knowledge of the action of alkyl halides. It would seem that silver formanilide, for example, reacts giving an acyl derivative, as follows :

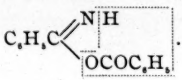
[1] Pinner, in his work "Die Imidoäther," states that an attempt to replace the imide hydrogen in benzimidoisobutylester by heating the ester to 100° with ethyl iodide led to no result. He obtained an abundant separation of cyaphenin with a small amount of resin. This result was probably due to the fact that Pinner's ester was not purified by distillation under diminished pressure. When these esters are thus purified some of them do not decompose but can be distilled at ordinary pressure, as shown by Bushong (This JOURNAL, 18, 490) and in previous papers from this laboratory.

[2] Wheeler and Boltwood : This JOURNAL, 18, 381; Wheeler and McFarland: *Ibid.*, 18, 540; Wheeler : *Ibid.*, 18, 695; Wheeler and Walden : *Ibid.*, 19, 129; Wheeler and Metcalf : *Ibid.*, 19, 217; Wheeler, Walden, and Metcalf : *Ibid.*, 20, 64.



A. B.

The first acyl derivative (A) being unstable, reacts further by addition as above (B), then acetyl chloride separates, the stable form, $O{=}C(H){-}N(COCH_3){-}C_6H_5$, results. The curious fact that silver benzamide gives with benzoyl chloride benzonitril and benzoic acid, and not dibenzamide, confirms this supposition. The first reaction of the silver salt is a direct replacement of silver by the acyl group. This arrangement being unstable the compound formed decomposes as follows :



It may, however, be stated in general that compounds of the formula $ROC(R'){=}NR''$ are more or less unstable, and readily pass into the isomeric form $O{=}C(R'){-}N(R''){-}R$. The ease with which this takes place depends on the character of the groups R, R′, and R″. It is therefore not improbable that with suitable groups and the proper regulations of conditions pseudoamides, $R'C(NR)OH$, and imidoacylanhydrides, $R'C(NR'')OCOR'$, which at present are unknown among acyclic compounds, may be prepared.

Experimental Part.

N-Ethylformanilide from Silver Formanilide.—25 grams silver formanilide dried over sulphuric acid and which on analysis gave 47.36 per cent. of silver (calculated 47.41 per cent.),

were heated with 22 grams of ethyl iodide[1] to 95°–100° for six hours. An oil resulted which was extracted from the silver iodide by means of dry ether. This gave, on distilling, a product boiling from 257°–267°. (Ethyl phenylimidoformate boils from 213°–215° at ordinary pressure.) This oil was twice distilled. It evidently decomposes to some extent. Two fractions were finally obtained. The first, which was clear and colorless, boiled from 259°–263°; the second from 263°–266° (barometer 772 mm.), the whole material boiling within 7° except a small residue left in the distilling-bulb. The absence of ethyl phenylimidoformate was shown, not only by the boiling-point of the material, but also, by mixing with ortho- and paratoluidine, when no amidines were found. A nitrogen determination in the clear, colorless, inodorous oil (no isonitril odor hence entire absence of formanilide) gave:

	Calculated for $HCONC_8H_8.C_6H_5$.	Found.
N	9.40	9.70

The material is therefore isomeric with the expected ethyl phenylimidoformate. Pictet and Crépieux[2] give the boiling-point of ethylformanilide as 258° at 728 mm. The fact that our material boiled, for the most part, higher than this is due to the difference in barometric pressure.

That our material was ethylformanilide is shown by the fact that on warming with hydrochloric acid and a little alcohol the formyl group separated as ethyl formate, and the resulting solution, on evaporation to dryness, gave a crystalline residue which, when pressed on paper and dried in the air, melted (not sharply) at 173°. Reynolds[3] states that the melting-point of ethylaniline hydrochloride is from 172°–175°. This, on dissolving in ice-water gave, with potassium nitrite, the characteristic nitroso-compound of ethylaniline. There is, therefore, no doubt, that the entire reaction-product was ethylformanilide.

[1] In the experiments in closed tubes we invariably weighed our ethyl iodide in a thin glass tube, which was sealed up as soon as weighed. This, with the imido-ester, was introduced into the larger tube used in heating, and, after this tube had been sealed and cooled, the smaller tube was broken by shaking. In this way we avoided loss by evaporation, and the otherwise unavoidable separation of iodine that always accompanies the sealing of tubes containing ethyl iodide.

[2] Ber. d. chem. Ges., **21**, 1108. [3] Jour. Chem. Soc., **61**, 455.

In order to determine whether the silver salt of formanilide reacts more readily with ethyl iodide than the imido-ester under the conditions of the reaction in the closed tube, we heated 15.45 grams of silver formanilide with 9.6 grams of ethyl iodide (about 1 gram less than molecular proportions) to the same temperature and for the same length of time as in the previous experiment. This gave an oil, but not a trace came over at the boiling-point of the imido-ester. It began to boil at about the same temperature as the product of the previous experiment, but the quantity was too small to give a constant boiling-point. The first few drops that came over were mixed with aniline when about sufficient diphenylformamidine for a melting-point determination was obtained. This shows that ethyl phenylimidoformate is more readily acted on in closed tubes than the silver salt.

In another experiment 25 grams of silver formanilide, the same preparation as that used above, and considerable excess of ethyl iodide, were warmed in ether for three days on the water-bath; not all the salt was acted on at this time, but, nevertheless, we obtained about 8 grams of ethyl phenylimidoformate, boiling from 213°–217°. The higher boiling material was by far the smallest part. This, decomposed with hydrochloric acid and evaporated to dryness, gave a solid mass which was taken up in water, filtered from resin, and then nitrous acid precipitated the nitroso-compound of ethylaniline. It seems, therefore, that ethyl phenylimidoformate suffers rearrangement, to some extent, at ordinary pressure and at the temperature of boiling ether.

N-Ethylbenzamide from Ethyl Imidobenzoate.—10 grams of ethyl imidobenzoate and 16 grams of ethyl iodide were sealed up and heated to 100° for eight hours, then two or three hours at 130°–160°. The contents of the tube, after evaporation of the ethyl iodide, distilled almost entirely from 176°–184° at 20–21 mm. pressure. A few drops distilled below 176°. This proved to be benzonitril. The chief product, weighing about 7 grams, was redistilled at ordinary pressure, when it practically all boiled from 295°–296°. This perfectly colorless oil deposited some crystals. The whole was then taken up in

benzene and filtered from a small amount of material crystallizing in plates and melting from 123°–126° (benzamide (?)). The benzene solution was evaporated and the oil redistilled. It boiled from 295°–298° and, on standing over night, deposited a mass of thick, colorless prisms. These, pressed on paper and freed from a little inodorous oil, melted from 69°–70°.

(The oil is perhaps $C_6H_5C\begin{matrix}NC_2H_5\\ \diagup\!\!\diagdown\\ OC_2H_5\end{matrix}$ or $C_6H_5C\begin{matrix}N\begin{matrix}C_2H_5\\ \diagup\\ \diagdown\\ C_2H_5\end{matrix}\\ \diagup\!\!\diagdown\\ O\end{matrix}$. It will be investigated later). The material was crystallized from dilute alcohol when beautiful, long, flattened, colorless prisms developed from the oil which first separated. These melted at about 69°. The melting-point of ethylbenzamide is usually given as 68°–69°. A nitrogen determination gave the result I below.

In another experiment, when an excess of imido-ester was used, the quantity of ethyl iodide being in the proportion of 2 molecules of the ester to 1 molecule of the iodide, the chief product boiled from 298°–299°. This was analyzed without being allowed to stand. It was free from crystals at first, but on standing solidified. The result on analysis (II below) shows that it is practically identical with the solid I.

	Calculated for $C_6H_5CONHC_2H_5$.	Found. I.	II.
N	9.40	9.11	9.47

The melting-point, appearance, behavior, and analysis therefore agree with those of ethylbenzamide, but Gattermann and Schmidt[1] give the boiling-point of this compound as 256°-260°. To settle this point we prepared ethylbenzamide by the Schotten-Baumann reaction and found that with 14 grams of material the entire product boiled at 762 mm. pressure from 298°–300°. This material is identical with the product from ethyl imidobenzoate in all its properties and the boiling-point given by the above authors is far from correct.

A quantitative determination of the products formed in the latter of the above experiments was made as follows: When 15 grams of ethyl imidobenzoate (2 molecules) were heated in

[1] Ann. Chem. (Liebig), **244**, 50.

a closed tube with 7.85 grams of ethyl iodide (1 molecule) for eight hours, a somewhat thick oil or solution resulted which contained minute crystals in suspension. The contents of the tube were diluted with dry ether and the turbid solution filtered. The melting-point of the needles, after they were washed with ether, showed that the material was a mixture or impure. It showed signs of melting at 120° and was completely melted at 203°. It had the appearance of cyaphenin. The quantity of this material was insignificant, less than 0.2 gram. On evaporating the ether solution an oil was obtained which was distilled at 18–19 mm. pressure. Three portions were then obtained: (1) below 170°, 1 gram; (2) 170°–178°, 9.1 grams; and a residue in smaller quantity above 178°, which soon solidified on cooling.

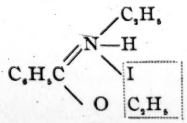
The first fraction proved to be mostly benzonitril; the second or greater portion was redistilled at 762 mm. pressure, when it practically all boiled from 298°–299°. It was obtained as a strongly refracting colorless oil which, on standing, soon solidified, but not completely, giving beautiful large crystals of ethylbenzamide. The residues from this distillation and that from the distillation under diminished pressure were dissolved in ether and the ether then evaporated. This residue weighed 4.5 grams. It appeared to consist of a mixture of benzamide and ethylbenzamide. It melted at about 60°. The material, crystallized from benzene, melted from 120°–126°. On crystallizing from water it separated in the form of plates and melted at 128°. The quantities of the different products, formed in the above experiment, is therefore about as follows:

	Grams.
Benzamide and ethylbenzamide,	4.5
Ethylbenzamide (and diethylbenzamide (?))	9.1
Benzonitril,	1.0
Cyaphenin,	0.2

From this it is apparent that the chief reaction is a rearrangement of the ethyl group from oxygen in the imido-ester to the nitrogen.

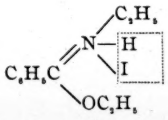
The formation of benzamide is to be explained by the decomposition of ethyl imidobenzoate hydriodide, which is

known to decompose into ethyl iodide and benzamide when heated. The formation of this ethyl imidobenzoate hydriodide is due to the separation of hydriodic acid from the addition-product which, as above stated, must be formed as an intermediate product. The reaction of ethyl iodide on ethyl imidobenzoate, therefore, proceeds in two ways, or in other words, the primary addition-product separates chiefly ethyl iodide (Fig. I below), and, to a lesser extent a portion decomposes separating hydrogen iodide (Fig. II), which then unites with the unaltered imido ester :



I.

and



II.

The ethyl ethylimidobenzoate resulting from the decomposition II is then rearranged with ethyl iodide yielding diethylbenzamide, or remains unaltered, so that one or both of these compounds constitute the oil which accompanies, in small amount, the crystals of ethylbenzamide.

Diethylbenzamide is known to be an oil. The other compound, ethyl ethylimidobenzoate, has not yet been prepared.

We are now engaged in preparing this and similar compounds, in order to determine more positively what the by-products in these reactions are, and we intend to examine the rearrangement of other imido-esters, in general, more thoroughly. We wish to reserve this field for ourselves.

NEW HAVEN, CONN., Nov. 1, 1898.

LXIX.—ON AN ISOMER OF POTASSIUM FERRICYANIDE.

BY JAMES LOCKE AND GASTON H. EDWARDS.

The behavior of potassium ferricyanide toward powerful oxidizing agents has been virtually but once the subject of investigation. In 1869 Städeler,[1] in support of his theory

[1] Ann. Chem. (Liebig), 151, 1.

that the iron in sodium nitroprussiate, $Na_2Fe(CN)_5NO_2$, is tetravalent, sought to obtain the related perferricyanide, $K_2Fe(CN)_6$, by the action of iodine upon the ferricyanide. He thus obtained a greenish-brown, crystalline product, which was apparently too impure for analysis, for he assigned the above formula to it without having quantitative data upon which to base his conclusions. A body having approximately the same characteristics as Städeler's compound was afterward obtained by Bong,[1] by the action of potassium chlorate and sulphuric acid upon the ferricyanide. To this product was likewise assigned the formula $K_2Fe(CN)_6$, but it could be prepared only in admixture with a large percentage of potassium sulphate, and no analysis of it was made. The principal work upon the subject, and the only work in which analytical results were obtained, was performed by Skraup in 1877. The latter, to a certain extent, adopted Bong's method, but he substituted hydrochloric acid for sulphuric, and isolated his reaction-product by repeatedly precipitating the aqueous solution with alcohol. He finally obtained a completely amorphous, black or dark-violet powder, which was intensely hygroscopic and smelled strongly of cyanogen. This body Skraup submitted to thorough analysis, but he was unable to obtain satisfactory results. The percentage of cyanogen fell much below the amount calculated for the compound $K_2Fe(CN)_6$ (about 4.0 per cent.). But the iron and potassium, while correspondingly high, were present in the approximate ratio of one to two, and he therefore assumed the body possessed the formula previously suggested by Städeler and Bong.

The details of the method of preparation used by Skraup were briefly as follows: Assuming the reaction to proceed in the simplest manner, *viz.*, according to the equation,

$$6K_4Fe(CN)_6+KClO_3+6HCl=6K_3Fe(CN)_6+7KCl+3H_2O,$$

he added to the hot solution of 50 grams potassium ferricyanide and 4 grams of potassium chlorate, in 100 cc. water, the calculated quantity of hydrochloric acid (4 grams, sp. gr. 1.19) in about 75 cc. water. The solution quickly assumed

[1] Bull. Soc. Chim. (1875), **24**, 268.

a peculiar red color, and after a few minutes effervescence was observed, presumably escaping cyanogen chloride. Shortly afterwards the solution was cooled down and allowed to stand for twenty-four hours. Precipitation with alcohol then yielded a crystalline product, which was redissolved in water and reprecipitated with alcohol about twelve times. On the third or fourth repetition of this operation the body began to lose its crystalline nature, and the final product, which he used for his analyses, was completely amorphous. The most characteristic reaction of the new compound, and the only one which indicated that its iron was in the tetravalent state, was found to be its decomposition by alkalies. On being boiled with the latter it yielded ferric hydroxide, potassium ferrocyanide, and potassium cyanate.

The method employed by Skraup is open to criticism at two points. If the reaction proceeds as he supposed, it should be stopped before the evolution of cyanogen chloride begins, for this must be due to the decomposition of the substance. In describing the reactions of the salt, Skraup states that it is slowly decomposed by alcohol. It would hardly seem advisable, therefore, to employ repeated precipitation with alcohol as a means of purifying it. These considerations led us to believe that the final, amorphous body was simply a decomposition-product of the supposedly impure crystalline precipitate obtained on the first addition of alcohol to the oxidized solution, and that this body might perhaps be obtained in a state more suitable for analysis by some other supplementary process.

We therefore prepared this salt according to Skraup's directions, but placed the mixture in ice-water as soon as the first sign of effervescence was observed. The time required for the reaction varies greatly with the temperature. When the hydrochloric acid is added to the boiling solution the gas comes off at once, but at 95°, the temperature at which we worked, about five minutes are required. When the solution had cooled to almost 20° it was filtered, and slightly less than an equal volume of alcohol, or just enough to bring about incipient precipitation, was added. The solution was

then allowed to stand until its temperature had fallen nearly to 0°. A dense crystalline precipitate separated out, from which the mother-liquid was drawn off as completely as possible, without washing, on a suction filter. The product was then redissolved in as little water as possible, and partially reprecipitated with a much smaller volume of alcohol. On a second repetition of this operation, the crystalline nature of the precipitate became less distinct, as Skraup also observed. The purification was therefore carried no further. The salt was extremely soluble in water, yielding a solution which was green by reflected light, and by transmitted light had a peculiar reddish tint. Thus far it corresponded with Skraup's observations, but on boiling with ammonium hydroxide it gave only a trace of ferric hydroxide and potassium ferrocyanide,[1] indicating that our supposition was correct, that Skraup's body was a product of decomposition of his first precipitate.

The salt obtained on the third precipitation with alcohol (the yield was about 1 gram) was carefully examined under the microscope for impurities. It consisted of very small, greenish-yellow needles, among which no foreign ingredients could be seen. The body was, therefore, subjected to analysis, in the expectation that it would give results corresponding closely with the formula $K_3Fe(CN)_6$. To our surprise, however, we found that, together with 11.83 per cent. of water, it contained the four elements in the same ratio as potassium ferricyanide itself, corresponding almost exactly with the formula $K_3Fe(CN)_6$. The results of this first analysis (I) follow:

	Calculated for $K_3Fe(CN)_6$ with 11.83 per cent. H_2O.	Found.	Ratio.	
H_2O	11.83	11.83	....	....
Fe	15.01	15.43	0.344	1.03
C	19.30	19.20	1.97	5.91
N	22.51	22.70	2.07	6.21
K	31.35	31.60	1.0	3.0
	100.00	100.76		

[1] A quantitative determination of the ferrocyanide thus formed by titration with potassium permanganate, showed that only 0.07 per cent. of the salt had undergone reduction.

The water present we afterwards found to be due chiefly to the extreme difficulty with which the salt can be dried. On precipitation the latter comes down as a network of very fine, delicate needles, in the capillary spaces between which the water is most obstinately retained. By allowing the salt to stand for several days in a vacuum over sulphuric acid, the percentage of water can be reduced until it corresponds with the value calculated for the formula $K_3Fe(CN)_6+H_2O$.[1] Our first supposition was that the presence of this water was the cause of the difference between the new compound and the normal ferricyanide, or, in other words, that it was water of constitution. This hypothesis, however, is inadmissible; for the corresponding silver salt, which can readily be obtained, is like normal silver ferricyanide—an anhydrous compound, and has the formula $Ag_3Fe(CN)_6$. The salt must, therefore, be regarded as an actual isomer of potassium ferricyanide. What the structural difference between the two is, or how the isomer happens to be formed through the action of such a substance as chloric acid, we cannot explain. But repeated analyses of the compound itself, and also of the silver salt, together with the quantitative study of reactions in which it was completely converted into the normal ferricyanide, leave no doubt as to its composition. Its reactions, on the other hand, are in some cases totally different from those of the latter compound. We propose for it, as a temporary designation, the term potassium β-ferricyanide.

The various analyses of the isomer published below were made from as many different preparations obtained under as varied conditions as possible. In the course of the work it was found that two precipitations with alcohol are sufficient to yield the body in a state pure enough for analysis. Even on the first precipitation it is nearly pure, giving no ferric hydroxide when boiled with ammonia and containing only a trace (about 0.5 per cent.) of chlorine. By using somewhat less than an equal volume of alcohol on the second precipitation, a yield of about 15 grams could be obtained, and when the conditions were very carefully observed the individual

[1] Found, 5.55 per cent. The theory requires 5.18 per cent.

crystals were large enough to be observed by the naked eye. A slight variation of the conditions in any particular, however, leads to the formation simply of a crystalline paste, which it is almost impossible to purify. The properly prepared salt can be easily and thoroughly washed with 75 per cent alcohol; when placed in a vacuum, after subsequent washing with absolute alcohol, it falls to an extremely light, voluminous powder. This possesses a pure, rich olive color, which appears brown when observed by gaslight. It dissolves with the utmost ease in water, but unlike Skraup's compound, it is not noticeably hygroscopic. The solution is comparatively stable, though it undergoes gradual decomposition on standing. This decomposition is not accompanied by the formation of either potassium cyanide, hydrocyanic acid or free cyanogen, nor does the dry salt possess the slightest odor of the latter substance.

Various attempts were made to obtain the salt in the form of larger crystals, by the evaporation of its concentrated aqueous solution. But owing to the capillary action of the needles as they separated on the sides of the vessel, only a dense efflorescent growth was obtained, from which no individual crystals could be isolated. Analysis II below is from one of these crops. When a small quantity of the salt is dissolved in a drop or two of water and allowed to crystallize out on an object glass, it is obtained as an intimate network of microscopic needles, of characteristic, very slightly tapering form. They are probably rhombic, showing parallel extinction, and slightly pleachroitic. Among them no trace of the heavy prismatic or block-shaped crystals of the normal or α-ferricyanide could be detected. In crystallization experiments with mixtures of the two isomers, on the other hand, they could be distinguished at a glance, showing that the new compound is not merely the α-ferricyanide in a new crystallographic modification.

Analytical Results.—For the determination of potassium and iron the compound was decomposed by heating with concentrated nitric acid. The iron was then precipitated with ammonium hydroxide, and the potassium weighed as chloride or

sulphate. The nitrogen was determined by combustion. The total combustion of the carbon takes place with great difficulty, and the results for that element were rather low (one per cent or more). In view of the above determination, (I) however, together with experiments on the quantitative conversion of the compound into potassium α-ferricyanide, its further determination was deemed unnecessary, and the percentage of cyanogen was calculated from that of the nitrogen. The water was determined by combustion.

	II.		III.	
	Found. Per cent.	Ratio.	Found. Per cent.	Ratio.
CN	45.31	6.0	45.13	6.15
Fe	16.95	1.04	16.02	1.01
K	33.91	3.00	32.90	3.00
H_2O	5.41	1.00	4.65	0.8
	101.47		98.70	

	IV.			
	Found.	Ratio.	Average of the 3 analyses.	Calculated for $K_3Fe(CN)_6.H_2O$.
CN	45.05	5.94	45.16	44.96
Fe	16.98	1.05	16.65	16.14
K	34.11	3.0	33.64	33.72
H_2O	4.73	0.87	4.93	5.18
	100.87		100.38	100.00

A subsequent determination of water, according to the method of Jannasch and Locke,[1] in another preparation which had previously been allowed to stand in a vacuum over sulphuric acid for three days, gave 5.55 per cent. There seems to be no doubt, therefore, that the body possesses the formula $K_3Fe(CN)_6.H_2O$. In order to prove this definitely, however, and at the same time make a direct estimation of the cyanogen, a method was sought by which the body could be quantitatively converted to the α-ferricyanide. Preliminary experiments showed that it passed into potassium ferrocyanide upon reduction, but its titration on that principle, either according to the method of Mohr[2] or after reduction with ferrous

[1] Ztschr. anorg. Chem., 6, 174. [2] Ann. Chem. (Liebig), 105, 62.

hydroxide, gave no satisfactory results. The most convenient means of reduction we found to be sodium amalgam in alkaline solution. This converted the substance completely into the ferrocyanide, without the separation even of traces of iron. The ferrocyanide was then titrated with potassium permanganate in sulphuric acid solution. The details of the method were first worked out with potassium α-ferricyanide, and the best conditions found to be as follows: The solution of the salt (about 0.2 gram) in 100 cc. of water, was rendered slightly alkaline with sodium carbonate, and a piece of 5 per cent sodium amalgam was then added. During the reduction the solution was kept on the steam-bath. In the course of an hour or so the mercury was filtered off and the solution cooled and very slightly acidified with sulphuric acid. It was then titrated with a solution of permanganate until the red color of the latter remained for half a minute or more.

With potassium α-ferricyanide the following results were obtained:

1 cc. $KMnO_4$ solution = 0.00572 gram Fe = 0.0336 gram $K_3Fe(CN)_6$.

	$K_3Fe(CN)_6$ taken. Gram.	Cc. $KMnO_4$ solution used.	Cc. $KMnO_4$ calculated.
I	0.2596	7.65	7.72
II	0.2402	7.10	7.15
III	0.1926	5.70	5.71

The same method of procedure gave for the new compound the following results:

	$K_3Fe(CN)_6.H_2O$ taken. Gram.	Cc. $KMnO_4$ solution used.	Cc. $KMnO_4$ solution calculated.
I	0.1611	4.55	4.55
II	0.2520	7.20	7.11
III	0.1946	5.40	5.49
IV	0.2641	7.35	7.45
V	0.1427	4.10	4.04
VI	0.2208	6.30	6.26

In order to make sure that in these experiments only potassium α-ferricyanide remained in the solutions, or, in other words, that the conversion of the β-ferricyanide to the latter compound was absolutely quantitative, the amount of

α-ferricyanide which the solutions in V or VI contained was gravimetrically determined. This was accomplished by precipitating the titrated solutions with silver nitrate, and estimating the percentage from the silver, which was weighed as chloride. The results were very exact, the amount of silver found differing by little more than a milligram from that required by theory:

V. Found, 0.1347 gram Ag = 0.1367 gram $K_3Fe(CN)_6$.
Calculated, 0.1332 gram Ag = 0.1352 gram $K_3Fe(CN)_6$.

VI. Found, 0.2048 gram Ag = 0.2079 gram $K_3Fe(CN)_6$.
Calculated, 0.2061 gram Ag = 0.2092 gram $K_3Fe(CN)_6$.

The average percentage of cyanogen in the β-ferricyanide, as calculated from these six determinations, is 45.07. The theory requires 44.96 per cent.

Potassium β-ferricyanide, like the normal salt, yields characteristic precipitates with the solutions of most of the heavy metals. These have, in general, the same characteristics as the corresponding α-ferricyanides, and in some cases *pass over into the latter with extreme ease.* The less notable of these precipitates are collected briefly in the table below, in which, for the sake of comparison, the α-ferricyanides are also included. The reactions examined were brought about in 2 per cent solutions. In the case of silver, bismuth, stannic tin, and lead, the reactions will be discussed more fully, as they present characteristic points of difference between the two ferricyanic groups.

	β-Ferricyanides.	α-Ferricyanides.
Cd.	Dirty green, soluble in $(NH_4)_2CO_3$, HCl, insoluble in HNO_3.	Pale yellow, soluble in $(NH_4)_2CO_3$, HCl, insoluble in HNO_3.
Cu.	Yellowish-green, insoluble in HNO_3 or HCl.	Dark greenish-yellow, insoluble in HNO_3 or HCl.
Fe^{III}.	Dark yellow coloration, blue precipitate on boiling.	Dark red coloration, blue precipitate on boiling.
Fe^{II}.	Blue precipitate.	Blue precipitate.
Hg^{II}.	No precipitate.	No precipitate.
Co.	Dark red precipitate, insoluble in HCl or HNO_3.	The same.

	β-Ferricyanides.	α-Ferricyanides.
Mn.	Brown precipitate, insoluble in NH_4OH, HCl, or HNO_3.	The same.
Hg^I.	Yellowish-green, flocculent precipitate. Rapidly undergoes reduction on boiling, becoming blue.	Pale yellow, undergoes reduction only slowly on boiling.
Ni.	Dark yellowish-green, insoluble in HNO_3 or HCl.	Light yellow, same behavior.
Zn.	Yellowish-green, soluble in HCl, $(NH_4)_2CO_3$, insoluble in HNO_3.	Yellow, same behavior.

The β-ferricyanides of these metals, as is seen, resemble the α-compounds in nearly all particulars, being distinguished from them chiefly in having a more or less pronounced green color. It might be supposed, therefore, that they are identical with them, but colored by slight impurities. But the behavior of the salts of bismuth, stannic tin, lead, and silver shows that this is not the case. Bismuth α-ferricyanide is a very sparingly soluble, straw-colored precipitate, which is deposited even from very dilute solutions of potassium ferricyanide on addition of bismuth nitrate. It is likewise insoluble in concentrated nitric acid. *A solution of potassium β-ferricyanide, on the other hand, when freshly prepared, gives no trace of a precipitate with bismuth nitrate.* The solution assumes a slightly greenish tint, but even when concentrated remains otherwise unaltered for some time. On standing, and especially when exposed to the action of the direct sunlight, it deposits large granules of a black, crystalline compound, which we have not yet fully examined, but which is apparently bismuth ferrocyanide.

Stannic chloride, on the other hand, yields no precipitate with potassium α-ferricyanide, but precipitates the isomer completely. The resulting compound comes down as a slimy, pure green body, which is insoluble in either hydrochloric or nitric acid. We have, however, been unable to obtain it in a state suitable for analysis.

A comparative study of the lead salts was kindly under-

taken by Mr. H. A. North. While lead ferricyanide is not precipitated by potassium α-ferricyanide, under ordinary circumstances, it is much less soluble in water than either the latter compound or lead nitrate. When concentrated solutions of the two are mixed in the proper proportions it slowly separates out in large, dark-red crystals.[1] Mr. North made this salt by dissolving the calculated quantities, or 3 grams each, of potassium ferricyanide and lead nitrate in 7 cc. and 8 cc. of water, respectively. On allowing the mixed solutions to stand for a few minutes, he obtained more than a gram of well-crystallized lead ferricyanide. A similar experiment was then made, with exactly the same quantities, potassium β-ferricyanide being used instead of the α-salt. No crystallization took place, indicating that lead β-ferricyanide is much more soluble in water than its isomer. This solution was allowed to stand over night, and by morning, in addition to an efflorescent product, more or less of the normal lead α-ferricyanide had crystallized out, the β-ferricyanide having partially passed over into the latter compound. The solution then gave the usual straw-colored precipitate with bismuth nitrate, with which it had not reacted twelve hours before.

Various attempts were made to isolate the β-lead salt by other means, but without much success. The most satisfactory results were obtained by dissolving lead oxide in glacial acetic acid, and adding to the solution the calculated quantity of potassium β-ferricyanide, dissolved in 25 cc. of glacial acetic acid and 7 cc. of water. A green, amorphous precipitate separated out, which was readily soluble in water forming a greenish-red solution, and this yielded no precipitate with bismuth nitrate. An analysis of the product showed that it contained 49 per cent lead, and no potassium, but no simple atomic ratio was evident between the lead and nitrogen, which was somewhat low. It is probable, therefore, that the body was a mixture. An experiment made with potassium α-ferricyanide, in a similar manner, yielded a crystalline precipitate of the ordinary lead ferricyanide.

The most interesting β-ferricyanide of a heavy metal which

[1] Rammelsberg : J. prakt. Chem. (2), 39, 455.

we have obtained is the silver salt. This is thrown down quantitatively as a dark-brown, flocculent precipitate, which can be readily filtered and washed.[1] Its most marked characteristic is the ease with which it passes into the α-ferricyanide. This takes place simply when the precipitate, suspended in its mother-liquid, is heated to 100°. The conversion is indicated by the change in color to the bright orange of the α-ferricyanide. The silver salt was prepared for analysis by adding the potassium salt to a slight excess of silver nitrate, both being in ice-cold solution. The precipitate was washed with ice-water, then with alcohol, and finally with ether, to secure rapid drying, and then allowed to stand in a vacuum, without exposure to light. The results of the analyses were as follows:

	Calculated for $Ag_3Fe(CN)_6$.	Found. I.	II.
Ag	60.47	59.41	60.00
Fe	10.45	10.84	....
N	15.67	15.31	....

The readiness with which the silver salt passes into silver α-ferricyanide presented another means of ascertaining whether the conversion of the one ferricyanic group into the other is actually quantitative. Weighed quantities of the potassium salt were precipitated with silver nitrate in the cold, and one of the precipitates (I) then rapidly heated in its mother-liquid until it had assumed the orange-red color of silver α-ferricyanide. The silver in each of the precipitates was then determined, and found to be as calculated for the compound $Ag_3Fe(CN)_6$.

I. 0.2912 gram $K_3Fe(CN)_6.H_2O$ gave 0.2729 gram Ag.
calculated 0.2724 gram Ag.

II. 0.2470 " " gave 0.2291 gram Ag.
calculated 0.2307 gram Ag.

The filtrates were then very thoroughly examined for products other than potassium nitrate. The filtrate from (I) contained a trace of iron, which was precipitated and weighed. It amounted only to 0.15 per cent. of the potassium salt. In

[1] On drying it forms a light, brown powder.

neither filtrate could either hydrocyanic or cyanic acid be detected. The change which the silver salt undergoes on heating must therefore be assumed to take place without the formation of any substance other than silver α-ferricyanide, and to consist simply in a rearrangement of atoms in the molecule $Ag_3Fe(CN)_6$.

It was hoped that by acting on the silver salt with the calculated quantity of hydrochloric acid the free β-ferricyanic acid could be prepared. The solution obtained gave for the moment no precipitate with bismuth nitrate, showing that the β-acid had been formed, but the latter passed within a few minutes into the normal acid, and then into further decomposition-products. Efforts to prepare the salts of calcium and barium in the same way also failed, the normal ferricyanides being finally obtained.

In regard to the constitution of the β-ferricyanic group we have little to state. Any attempt to assign a definite structural formula to it would, for the present, be pure speculation. The suggestion offers itself that one of the two isomers contains isonitril groups, the other nitril groups. But this view, at least, is absolutely refuted by the identical behavior of the two on reduction. So far as we can find, there are no cases known where isomers containing respectively the —CN and —NC groups yield the same product with nascent hydrogen. On the other hand, if both ferricyanides contain only cyanogen groups, the β-compound becomes of especial importance because of its bearing on Werner's theory. According to the latter the ferricyanic group is not to be represented by the structural formula, but simply as a radical in which the cyanogen groups occupy "coordination positions" about the ferric atom. Isomerism between two equivalent $Fe(CN)_6$ groups, if this is so, can be due only to stereochemical causes. The greatest value of Werner's theory lies in the explanation which it offers of the cases of isomerism among the platinamine and cobaltiamine compounds. The six coordinated groups are supposed to occupy the angles of a regular octahedron, in the center of which is the metal. Isomerism is then possible whenever two or more of the coordinated groups

differ from the others. But according to it a radical in which they are all alike, such as $Fe^{III}(CN)_6$, cannot have two different configurations, or in other words, exist in isomeric modifications. It would seem, therefore, that the existence of potassium β-ferricyanide stands in direct contradiction to such a theory, at least in its present form.

It may of course be that the β-ferricyanide is a mixture of two substances in proportions giving the atomic ratio $K_3Fe(CN)_6$. But throughout all our investigations we have searched for, and failed to find, a single indication that such is the fact. Its completely crystalline and homogeneous appearance, the constant composition of different products, and all its observed reactions point closely to its being an individual chemical compound. Our investigations will be continued, however, and we hope to bring more light to bear upon the subject within a short time.

NEW HAVEN, December 12, 1898.

REACTION OF ORTHODIAZOBENZOIC ACID WITH SULPHUROUS ACID AND COPPER POWDER.

BY W. E. HENDERSON.

The work described in the following article was undertaken in the chemical laboratory of the Johns Hopkins University for the purpose of testing the truth of the statement not infrequently found in the literature, particularly in text-books and chemical dictionaries, that sulphonic acids result from the decomposition of diazo compounds in the presence of sulphurous acid, especially if copper powder or cuprous hydroxide is present in the solution.[1]

If such a reaction is a general one, it was thought to be desirable to ascertain the conditions most favorable for successfully employing it, as it would possess considerable interest from a theoretical as well as from a practical standpoint. For although there have been a number of methods devised for

[1] Watts' Dictionary: "Sulphonic Acids"; Meyer and Jacobson's Lehrbuch, II, 294; Bernthsen's Org. Chem. (McGowan's Trans.), p. 397; Hübner: Ber. d. chem. Ges., 10, 1715; Müller and Wiesinger: *Ibid.*, 12, 1348; Landsberg: *Ibid.*, 23, 1454.

introducing into an aromatic nucleus group containing sulphur, which can be converted into sulphonic acid residues, few of these methods are very satisfactory, and we are forced to depend, for the most part, on methods of direct sulphonation for obtaining sulphonic acids. This often leaves in doubt the question as to which position the entering group occupies, and a practical method for replacing any group of known position by a sulphonic acid group, would be of much interest in deciding cases of doubtful orientation by synthesis.

Many attempts have been made to replace an amido group, with some group containing sulphur by employing a diazo decomposition. The results have been quite varied and in general unsatisfactory; for although many definite products have been obtained, the main reaction has been complicated by many secondary ones, due to the reducing power of the sulphur compounds employed. Chief among these substances have been hydrogen sulphide,[1] alkali sulphides,[2] sulphurous acid,[3] mercaptans and sulphides,[4] and thiocarbonic ethers.[5] The products have been sulphides, hydrosulphides, or sulphonic acids in very small quantity, and the methods have not promised much in a practical way.

Gattermann,[6] in his paper on diazo decompositions in the presence of various free acids and copper powder, suggested that by employing sulphurous acid, sulphonic acids would probably result, but he did not subsequently follow up this suggestion.[7]

Preliminary experiments showed that, under ordinary circumstances at least, sulphonic acids do not result from this reaction, but other substances, difficult to isolate owing to their solubility, are formed. Hence orthoaminobenzoic acid was selected as the material for study, in the hope that the

[1] Tassinari: Gaz. chim. Ital., **22**, 504; Griess: Ann. Chem. (Liebig), **137**, 74.

[2] Graebe and Mann: Ber. d. chem. Ges., **15**, 1688; Griess: Ann. Chem. (Liebig), **137**, 74; Klason: Ber. d. chem. Ges., **20**, 349; Purgotti: Gaz. chim. Ital., **20**, 30.

[3] Hübner: Ber. d. chem. Ges., **10**, 1715; Müller and Wiesinger: *Ibid.*, **12**, 1348; Landsberg: *Ibid.*, **23**, 1454.

[4] Stadler: *Ibid.*, **17**, 2078.

[5] Leuckart: J. prakt. Chem. [II], **41**, 179.

[6] Gattermann: Ber. d. chem. Ges., **23**, 1218.

[7] After the results described in this paper had been obtained, the paragraph in Centralblatt, 1898, II, 196, came to my attention.

carboxyl group would render the product of the reaction easy to obtain and identify. This proved to be the case, and the product obtained was found to be dithiosalicylic acid, $[C_6H_4.COOH]_2S_2$.

On adding a solution of orthodiazobenzoic acid sulphate to a cold, saturated solution of sulphurous acid in which copper powder was suspended, nitrogen was at once evolved. The reaction was a very clean one, free from all the tarry products, which so often accompany reactions of this kind. Quite an amount of copper passed into solution as the reaction proceeded, forming a mixture of cuprous and cupric salts, and a part of the sulphurous acid was oxidized to sulphuric. The reaction is therefore accompanied by an extensive reduction, and instead of obtaining orthosulphobenzoic acid, dithiosalicylic acid is the chief product. It is probable that both the corresponding sulphinic acid and thiosalicylic acid could be obtained by suitable methods, but no effort was made to isolate them. The yield of dithiosalicylic acid was about 50 per cent. of the theoretical.

Inasmuch as the dithio-acid yields orthosulphobenzoic acid on oxidation with potassium permanganate, the main purpose in view was not entirely defeated by this unexpected result. I shall study the reaction further, both in the case of other amido compounds, which preliminary experiments show to act generally in the same way, and as to the yield of sulphonic acids that can be obtained by oxidation of the raw product.

EXPERIMENTAL PART.

Five grams orthoaminobenzoic acid were dissolved by warming in a solution of 6 grams sulphuric acid (sp. gr. 1.84) in 40 cc. water, and the solution was cooled to 5°. During the cooling the solution was constantly stirred so that the crystals of anthranilic acid sulphate which separated, might be as small as possible. To this solution was added slowly from a dropping-funnel, a solution of 3 grams sodium nitrite, until, after stirring for some time, the solution colored starch iodide paper, and all the crystals of anthranilic acid sulphate were dissolved.

The solution of orthodiazobenzoic acid sulphate so prepared was then added, from a dropping-funnel, to a cold, saturated solution of sulphurous acid (about 200 cc.) in which 30 grams of copper powder had been suspended. The solution was contained in a good-sized flask to facilitate constant shaking so that the copper might not settle to the bottom. Nitrogen was at once evolved, and the solution assumed an emerald-green color. On standing for some time or by heating on the water-bath, a voluminous, colorless precipitate was slowly thrown down, which proved to be dithiosalicylic acid. The precipitation was slow, and apparently incomplete, so that it was found best to obtain the acid in the following way:

After filtering off the excess of copper powder, barium carbonate was added to the hot solution as long as it produced a dark-colored precipitate, which first appears when most of the free acid has been neutralized. This appears to be, for the most part, the copper salt of dithiosalicylic acid, together with other copper compounds. The insoluble substances were filtered off and warmed with hydrochloric acid. This dissolved the excess of barium carbonate, the barium sulphite, and the copper compounds, and left the barium sulphate and the insoluble dithiosalicylic acid on the filter. On digesting the mixture with sodium hydroxide, the latter acid was dissolved with formation of its sodium salt, and the free acid was regained, as an amorphous precipitate, by pouring the filtrate from the barium sulphate into an excess of hydrochloric acid.

The chief reactions of this acid, together with the properties of its principal salts, its chloride, and its methyl and ethyl ethers have recently been described by List and Stein,[1] who obtained it by the reduction of the unsymmetrical chloride of orthosulphobenzoic acid, an account of whose work came to hand during the progress of this study. These details need not, therefore, be repeated here. The acid was fully identified by its agreement with their description and by an analysis.

I. 0.1880 gram substance gave 0.3770 gram CO_2, and 0.0567 gram H_2O.

II. 0.2428 gram substance gave 0.3720 gram $BaSO_4$.

[1] List and Stein: Ber. d. chem. Ges., 31, 1666.

	Calculated for $(C_4H_4COOH)_2S_2$.	Found.
C	54.90	54.63
H	3.26	3.35
S	20.91	21.06

The chloride crystallized from benzene in thick, yellow needles or prisms and melted at 154°. The methyl ester, made by boiling the chloride in methyl alcohol, melted at 131°.

My thanks are due to Dr. Stieglitz, of the Kent Laboratory at Chicago, for many courtesies shown me while working in his laboratory.

ATHENS, OHIO, December, 1898.

Contributions from the Chemical Laboratory of Purdue University.

DIRECT NITRATION OF THE PARAFFINS.

BY R. A. WORSTALL.

In a previous communication[1] were given the results of a preliminary investigation of the action of nitric acid upon the paraffins, showing that the action of nitric acid without pressure results in the formation of primary mono- and dinitro-paraffins, together with oxidation-products which, for the hydrocarbons studied, were found to be the same in all cases; namely, carbonic, acetic, succinic, and oxalic acids.

A more careful investigation of these reactions, repeating the experiments with the three hydrocarbons previously studied, and extended so as to include other paraffins, has been made, in order to ascertain the limits of the reaction, and the quantitative yield of nitro-products obtainable from each hydrocarbon, while more attention has been paid to the oxidation-products. This investigation has confirmed, in all essential particulars, the statements made in the preliminary paper.

The source of all the hydrocarbons studied has been American petroleum, all save one of them, either in the crude or refined state, having been secured through the kindness of Dr. C. F. Mabery. The method of purification has been the same

[1] This JOURNAL, 20, 202.

for each—namely, agitation with fuming sulphuric acid, washing with caustic soda, drying, and fractioning over metallic sodium, in many cases as often as thirty times, until a good separation was obtained.

Unless otherwise stated, the method of nitration has been in each case as follows: The hydrocarbon was boiled with nitric acid of proper concentration in a flask fitted with return-condenser, until the acid was exhausted. The spent acid was then drawn off and fresh acid added, the operation being repeated until a considerable quantity of the hydrocarbon appeared to have been converted into nitro-products. The oil was then drawn off, washed, dried, and the unchanged hydrocarbon distilled off, leaving the high-boiling nitro-compounds as a residue. The process was repeated with the unchanged hydrocarbon as long as necessary. The mixed nitroparaffins were separated by distilling in steam, in which only the mononitroparaffins are volatile. Oxidation-products were sought for in the escaping gases and in the spent acid.

Hexane, C_6H_{14}.

Normal hexane (boiling-point 68°–69°, specific gravity 0.6860 at $\frac{20°}{4°}$) reacts with fuming nitric acid and with mixed sulphuric and fuming nitric acids, but there is no apparent reaction when nitric acid of specific gravity lower than 1.45 is employed. Even with nitric acid of specific gravity 1.60 the reaction is very slow, but in time the hydrocarbon is completely transformed into nitro- and oxidation-products.

Two hundred and fifty grams hexane were treated with five successive portions of 200 grams each of fuming nitric acid, sp. gr. 1.60, being boiled with each portion eight hours. The loss through oxidation amounted to 70 grams, and the yield of mixed nitro-products to 13 grams. By continuing the nitration the average yield has been 10 per cent of the theoretical of mixed nitro-products, about 6 per cent nitrohexane, and 4 per cent dinitrohexane. Through a misprint (unfortunately overlooked until too late) the statement made in the preliminary paper in regard to the yield of nitrohexane was entirely wrong. No such yield as there stated (60 per cent) has been at any time obtained.

Oxidation-products.

Numerous tests have failed to show the presence of more than four oxidation-products—acetic, succinic, carbonic, and oxalic acids. In boiling these hydrocarbons with nitric acid there is a persistent odor of butyric acid noticeable in the spent acid, especially in the case of the higher-boiling paraffins. The dinitroparaffins have a butyric-like odor, and from inability to detect the presence of any fatty acid higher than acetic, it was concluded that the odor was due to these dinitroparaffins.

Acetic Acid.—A portion of the spent acid was neutralized with sodium carbonate, acidified slightly with sulphuric acid, and distilled in steam. Free nitrous acid in the distillate was destroyed by a dilute solution of potassium permanganate, and the distillate then neutralized with calcium carbonate, and filtered. Silver acetate was precipitated in the filtrate by means of silver nitrate, and the precipitate dissolved in hot water and crystallized. A silver determination showed the salt to be pure silver acetate.

0.0991 gram gave, on ignition, 0.0635 gram Ag.

	Calculated for CH_3COOAg.	Found.
Ag	64.67	64.09

Oxalic Acid.—Upon concentrating the spent acids on the steam-bath, and cooling, oxalic and succinic acids separated as crystals. The mixed acids were recrystallized several times from hot water, fine crystals of each being obtained pure. A portion of the oxalic acid was converted into the calcium salt and the latter analyzed.

0.3151 gram gave 0.1360 gram CaO.

	Calculated for CaC_2O_4.	Found.
Ca	31.25	30.83

Succinic Acid.—The succinic acid was easily identified by its melting-point (176°) and by many qualitative tests. Its ammonium salt gave a white precipitate with alcoholic barium chloride, and a red-brown precipitate with ferric chloride in the cold.

Carbonic Acid.—Carbonic acid was detected in the gases es-

caping from the nitration-flask, by the formation of precipitates with solutions of barium and of calcium hydroxides.

The total yield of oxidation-products other than carbonic acid did not exceed 5 per cent. The latter, however, must have formed by far the chief product of the reaction.

Heptane, C_7H_{16}.

The heptane employed was the normal hydrocarbon (boiling-point 98°–99°, specific gravity 0.6980 at $\frac{20°}{20°}$).

Nitric acid of specific gravity 1.42, mixed sulphuric and nitric acids, and fuming nitric acid all react with heptane to form nitro-derivatives. The nitric acid of specific gravity 1.42 gives the best yield of mononitroheptane, the action of the mixed acids resulting in the formation of considerable dinitroheptane, that of the fuming nitric acid in greater oxidation.

The method of nitration and of separating the products was the same as before described. Three hundred and fifty grams heptane treated for ninety-four hours with 1200 grams nitric acid (1.42 sp. gr.) gave 80 grams nitroheptane, 16 per cent of the possible theoretical yield, and 90 grams of dinitroheptane, 24 per cent of the possible theoretical yield, the total yield of nitro-products, therefore, amounting to 40 per cent of the theoretical.

The oxidation-products were the same as in the case of hexane.

Acetic Acid.—The acetic acid was separated from a portion of the waste acids in the manner previously described. The silver salt was analyzed.

0.0473 gram gave, on ignition, 0.0305 gram Ag.

	Calculated for CH_3COOAg.	Found.
Ag	64.67	64.50

Oxalic Acid.—Oxalic and succinic acids were separated from the waste acids and from each other in the manner previously described. The calcium oxalate was analyzed.

0.0480 gram gave, on ignition (with sulphuric acid), 0.0511 gram $CaSO_4$.

	Calculated for CaC_2O_4.	Found.
Ca	31.25	31.45

Succinic Acid.—The succinic acid was recognized by its melting-point and the qualitative tests mentioned under hexane.

Carbonic Acid.—Carbonic acid was detected by the usual test in the gases escaping from the nitration-flask. It must have constituted fully 70 per cent of the total products, the other oxidation-products not appearing to exceed 5 per cent.

Octane, C_8H_{18}.

Normal octane (boiling-point 123°–125°, specific gravity 0.7123 at $\frac{20°}{4°}$) reacts with nitric acid of specific gravity as low as 1.070 with the formation of nitro-products. Nitric acid of specific gravity 1.14 gave the best results, as a larger yield of nitrooctane can be obtained by acid of this concentration, and with less oxidation than by using more concentrated acid. Two hundred and eighty grams octane treated for forty-two hours with 1100 grams of this acid gave 70 grams nitrooctane, 17.5 per cent of the possible theoretical yield, and 125 grams dinitrooctane, 25 per cent of the possible theoretical yield, a total of 42.5 per cent of the theoretical.

The usual oxidation-products resulted.

Acetic Acid.—The acetic acid was separated as described under hexane, and the silver salt analyzed.

0.0457 gram gave, on ignition, 0.0296 gram Ag.

	Calculated for CH_3COOAg.	Found.
Ag	64.67	64.75

Oxalic Acid.—Oxalic and succinic acids were obtained from the spent acid in the manner previously described. The calcium oxalate was analyzed.

0.2743 gram gave 0.1190 gram CaO.

	Calculated for CaC_2O_4.	Found.
Ca	31.25	30.98

In all, 10 grams of oxalic acid were obtained from the 280 grams octane.

Succinic Acid.—The succinic acid was readily recognized by its melting-point (175°) and by its qualitative reactions. About 3 grams of succinic acid were obtained.

Carbonic Acid.—The carbonic acid was detected in the usual way, and must have been equivalent to nearly 60 per cent of the total product, the other oxidation-products not exceeding 5 per cent.

Nonane, C_9H_{20}.

The nonane employed was the normal hydrocarbon (boiling-point 150°–151°, specific gravity 0.7277 at $\frac{20°}{20°}$). Even very dilute nitric acid acts upon nonane with the formation of nitro-derivatives. For the preparation of nitrononane, nitric acid of specific gravity 1.080 was employed, the method of nitration and of separating the products being the same as previously described. Two hundred and sixty-eight grams nonane treated for forty-two hours with 1200 grams of nitric acid of specific gravity 1.080 gave 80 grams nitrononane, 22 per cent of the possible theoretical yield, and 210 grams dinitrononane, 48 per cent of the possible theoretical yield, a total yield of nitro-products amounting to 70 per cent of the theoretical.

As usual, the oxidation-products were acetic, carbonic, succinic, and oxalic acids.

Acetic Acid.—The acetic acid was separated in the usual way and the silver salt analyzed.

0.0652 gram gave, on ignition, 0.0418 gram Ag.

	Calculated for CH_3COOAg.	Found.
Ag	64.67	64.11

Oxalic Acid.—The calcium salt of the oxalic acid was analyzed.

0.3334 gram gave 0.1450 gram CaO.

	Calculated for CaC_2O_4.	Found.
Ca	31.25	31.07

About 4 grams of oxalic acid were obtained from the 268 grams nonane.

Succinic Acid.—Much more succinic acid was formed from

nonane than from any other hydrocarbon. Each time, upon cooling the spent acid in the nitration-flask, considerable succinic acid crystallized out, in all about 7 grams being obtained.

Carbonic Acid.—Carbonic acid was detected as usual in the escaping gases, and probably did not exceed 30 per cent. of the total products.

Decane, $C_{10}H_{22}$.

The decane employed was the normal hydrocarbon,[1] (boiling-point 175°, specific gravity 0.7398 at 20°). Fuming nitric acid and mixed sulphuric and nitric acids, are without action upon decane in the cold. When heated, however, quite dilute nitric acid will nitrate the hydrocarbon, acid of specific gravity 1.080 giving the best results. The instability of nitrodecane at the temperature of boiling decane prevented the employment of the method previously followed for the separation of the nitro-products. The layer of oil was separated from the spent acid, washed well, then dried, and thin strips of metallic sodium added. By this means all nitroparaffins were slowly converted into sodium salts. The latter were washed out with water, and the residual paraffin again nitrated. For the separation of the nitroparaffins from their salts, the method of Konowalow[2] was employed. The aqueous solution of the sodium salts was saturated with carbon dioxide, the liberated nitroparaffins extracted with ether, and the ether distilled off. By distilling this mixture of mono- and dinitrodecane in steam, the former was obtained pure, but the dinitrodecane decomposed. Twenty grams decane, treated for twelve hours with nitric acid of specific gravity 1.080, without attempting to convert all the hydrocarbon into nitro-products, gave 10 grams nitrodecane, about 35 per cent of the theoretical yield. With larger quantities of the hydrocarbon, carrying the reaction to completion, better yields could no doubt be obtained.

Hendecane, $C_{11}H_{24}$.

Hendecane (boiling-point 196°,[3] specific gravity 0.7521 at

[1] Mabery: This JOURNAL, 19, 448. [2] *Loc. cit.*
[3] Mabery: *Loc. cit.*

20°) is not acted upon by fuming nitric acid in the cold. When gently boiled with nitric acid of specific gravity 1.080, nitration readily results. Twenty grams hendecane were heated for six hours with 100 grams of 1.080 nitric acid, and the nitroparaffins separated as described under decane. While not all the hydrocarbon had been nitrated by this treatment, nearly 8 grams of nitrohendecane were obtained, and the dinitroparaffin was decomposed.

Dodecane, $C_{12}H_{26}$.

Dodecane (boiling-point 216°)[1] is slowly acted upon by fuming nitric acid in the cold, with the formation of nitro-products. Twenty-five grams of the hydrocarbon were heated with 100 grams of nitric acid (specific gravity 1.080) for six hours. The nitroparaffins were separated as in the case of the two preceding hydrocarbons. The nitrododecane as obtained by distilling in steam was impure, containing some free hydrocarbon, and the quantity obtained was too small to permit purification. In the case of the last three hydrocarbons, no attention was paid to oxidation-products because of the doubtful purity of these higher distillates of petroleum.

Francis and Young,[2] in giving the results of their study of the action of fuming nitric acid upon petroleum distillates, state that normal nitroparaffins could not have been formed to any appreciable extent, for on diluting the spent acid no nitro-compounds were precipitated. As a matter of fact, the nitroparaffins thus formed are not to be found in the spent acid. In the course of this work it has frequently been noted that when even from 50 to 75 per cent of the hydrocarbon had been converted into nitroparaffins, the latter still floated as an oily layer above the acid, and upon diluting the latter no more than traces of nitro-compounds were precipitated, the latter invariably being dinitroparaffins.

Acetic, succinic, oxalic, and carbonic acids would seem to be the normal products resulting from the oxidation of any paraffin by nitric acid. Even after 75 per cent of the original hydrocarbon had been converted into nitro- and oxida-

[1] Mabery: *Loc. cit.* [2] Jour. Chem. Soc., 1898, 928.

tion-products, the residual paraffin, when boiled with nitric acid, still gave the same oxidation-products. This fact would seem to show that the latter are not due to the oxidation of naphthenes or other foreign hydrocarbons.

LAFAYETTE, IND., Dec., 1898.

HIGHER PRIMARY NITROPARAFFINS.

BY R. A. WORSTALL.

To Victor Meyer and his pupils we are indebted for most of our knowledge of the nitroparaffins from nitromethane to nitropentane, inclusive. These lower nitroparaffins are readily obtained by Victor Meyer's method, the action of silver nitrite on the alkyl iodides, and their properties and derivatives have been well worked out.

Of the primary nitroparaffins above nitropentane, however, but few have ever been made, and even of these little is known. Two causes have operated to make the preparation of the higher nitroparaffins exceedingly difficult. The first is the extreme difficulty attendant upon the preparation of the alkyl iodides necessary for the reaction; and the second is the fact that even after this necessary material has been prepared, the yield of nitroparaffins is small, in consequence of the simultaneous formation of the isomeric nitrous ethers, while it seems almost impossible to free the nitroparaffins from these ethers. Nor are the items of time and expense inconsiderable obstacles to their preparation.

Chancel,[1] by the action of nitric acid on methylhexylketone, obtained dinitrohexane. Beilstein and Kurbatow,[2] by the action of nitric acid on a fraction of American petroleum boiling at 95°–100°, obtained what was doubtless nitroheptane. They attributed its formation to naphthenes. Eichler[3] prepared nitrooctane from octyl iodide and silver nitrite and studied its properties and a few of its derivatives. These seem to be the only recorded instances of the preparation of primary nitroparaffins above nitropentane.

[1] Compt. rend., **94**, 399. [2] Ber. d. chem. Ges., **13**, 2029.
[3] *Ibid.*, **12**, 1883.

Konowalow[1] has shown that when the paraffins are heated in sealed tubes with dilute nitric acid, secondary and tertiary nitroparaffins result. The preceding paper describes a method for the preparation of primary mono- and dinitroparaffins above and including nitrohexane, and by this method the nitroparaffins herein described were made. The reaction and derivatives described in this paper have been chiefly those which would help to establish the structure of the nitroparaffins. Other derivatives have been prepared and at least one new reaction noted, and these are retained for later papers.

Nitrohexane, $C_6H_{13}NO_2$.

The nitrohexane separated from the dinitrohexane by distillation in steam (page 211) was dried and fractioned. The greater portion distilled at 180°–181°, and analysis showed it to be pure.

0.2062 gram gave 22.0 cc. nitrogen at 741 mm. and 23°.

0.1154 gram gave 0.2316 gram CO_2, and 0.1010 gram H_2O.

	Calculated for $C_6H_{13}NO_2$.	Found.
C	54.96	54.73
H	9.92	9.74
N	10.72	10.93

Properties.—Nitrohexane is a nearly colorless liquid of pleasant, ester-like odor. Its boiling-point is 180°–181° (uncorr.); its specific gravity 0.9605 at 17°. It is insoluble in water, readily soluble in alcohol, ether, and other organic solvents. Like nitropentane[2] it is only very slowly soluble in concentrated aqueous solutions of caustic soda or caustic potash, thus differing from the lower nitroparaffins. It is readily soluble in alcoholic sodium or potassium hydroxide. It is not explosive. With potassium nitrite, sulphuric acid, and potassium hydroxide it gives the nitrolic acid reaction characteristic of primary nitroparaffins.

Sodium Nitrohexane, $C_6H_{12}NO_2Na$.—For the preparation of sodium salts of the lower nitroparaffins, V. Meyer[3] found two methods which gave pure products. The one was to dissolve

[1] Compt. rend., 114, 26. [2] V. Meyer: Ann. Chem. (Liebig), 171, 44.
[3] *Loc. cit.*, p. 29.

the nitroparaffin in alcohol and add alcoholic sodium hydroxide. The sodium salt being insoluble in alcohol is precipitated, and can readily be purified. The other method was to dissolve the nitroparaffin in benzene and add strips of metallic sodium. The salt thus formed was pure. The former method is not applicable to these higher nitroparaffins for the reason that all their alkaline salts are readily soluble in alcohol. And the second method is unsatisfactory. For while the action of the metallic sodium on the nitroparaffin in solution in benzene or petroleum ether gives the sodium salt, the latter is usually impure. The metallic sodium seems partially to decompose the nitroparaffin even in the cold, ammonia and sodium nitrite being among the products.

A method was found, however, which gave satisfactory results. The nitroparaffin is dissolved in petroleum ether, and to this solution is added a solution of sodium ethylate made by largely diluting an alcoholic solution of sodium ethylate with petroleum ether. The precipitated sodium salt, when filtered off and washed several times with boiling petroleum ether containing some alcohol, is usually pure.

Analysis of the sodium nitrohexane gave the following result:

0.1345 gram gave 0.0620 gram Na_2SO_4.

	Calculated for $C_6H_{12}NO_2Na$.	Found.
Na	15.03	14.93

Properties.—Sodium nitrohexane is a white salt, readily soluble in water and in alcohol, insoluble in ether, carbon disulphide, etc. It usually separates from solvents as a gelatinous mass, but can with difficulty be crystallized from alcohol in fine, silky needles. It blackens when heated but is not explosive.

With solutions of certain metallic salts, sodium nitrohexane gives characteristic results. The silver precipitate is yellow, rapidly turning black. Cupric sulphate gives a green precipitate. Mercuric chloride a yellow precipitate. With solution of ferric chloride an intense red coloration results. Konowalow[1] has shown this to be a characteristic reaction for all primary and secondary nitroparaffins.

[1] Ber. d. chem. Ges., 28, 1851.

Strong acids do not liberate the nitroparaffin from its sodium salt. While the reaction was not investigated it is doubtless analogous to that shown by Nef[1] to take place with sodium nitroethane.

Hexylamine, $C_6H_{13}NH_2$.—When nitrohexane is gently warmed with iron filings and dilute acetic acid, hexylamine is formed. More vigorous methods of reduction, such as boiling with iron and acetic acid, or with tin and hydrochloric acid, result in total or partial decomposition with the formation of ammonia. The same fact was noted by V. Meyer[2] in the reduction of nitroethane. The hexylamine liberated from the solution by adding caustic soda and distilling in steam was a strong base, giving the isonitril reaction for a primary amine. Its chlorplatinate is sparingly soluble in water. Analysis of the latter salt gave the following result:

0.0110 gram gave, by ignition, 0.0034 gram Pt.

	Calculated for $(C_6H_{13}NH_3Cl)_2PtCl_4$.	Found.
Pt	30.47	30.90

Action of Hydrochloric Acid.—As a primary nitroparaffin, nitrohexane, when heated with concentrated hydrochloric acid to about 125°, should yield hexoic acid and hydroxylamine, while secondary or tertiary nitroparaffins would yield resinous products.[3]

About 5 grams nitrohexane were heated in a sealed tube with 10 grams concentrated hydrochloric acid for two hours at 120°. The tube was then opened and the contents diluted with water. The reaction had proceeded smoothly without formation of any resinous products. The solution was neutralized with caustic soda, slightly acidified with acetic acid, and extracted with ether. The ether was distilled off and the residue diluted with water, boiled with calcium carbonate, and filtered. Silver hexoate was precipitated in the filtrate by means of silver nitrate, and this compound was analyzed.

0.0630 gram gave, on ignition, 0.0300 gram Ag.

[1] Ann. Chem. (Liebig), **280**, 263. [2] *Ibid.*, **171**, 27.
[3] V. Meyer and Locher: Ann. Chem. (Liebig), **180**, 164.

	Calculated for $C_5H_{11}COOAg$.	Found.
Ag	48.43	47.63

Dinitrohexane, $C_6H_{12}(NO_2)_2$.

The dinitrohexane left after distilling off all nitrohexane in steam is generally impure, as it is exceedingly difficult to drive over all nitrohexane without raising the temperature so high as partially to decompose the dinitrohexane. Occasionally, when separating the spent acid from the oil, a middle layer has been noticed. When separated, washed, and dried, this was found to be pure dinitrohexane.

0.3727 gram gave 55.0 cc. nitrogen at 741 mm. and 21°.

0.1511 gram gave 0.2251 gram CO_2, and 0.0911 gram H_2O.

	Calculated for $C_6H_{12}N_2O_4$.	Found.
C	40.90	40.65
H	6.82	6.67
N	15.91	15.94

Properties.—Dinitrohexane is a clear yellow oil of acid character, and of a sweet ester-like odor. It is heavier than, and somewhat soluble in, water. Readily soluble in alcohol, ether, etc. It cannot be distilled without decomposition. It is very slowly soluble in aqueous solution of sodium or potassium hydroxide, readily soluble in their alcoholic solutions with a red color.

With bromine water a heavy oily bromide is formed, which is insoluble in aqueous or alcoholic sodium hydroxide. Reduction with tin and hydrochloric acid yields ammonia as one of the products. These facts indicate that it is primary, but there was not enough at hand for more definite determinations.

Nitroheptane, $C_7H_{15}NO_2$.

The nitroheptane separated from the dinitroheptane by distillation in steam (page 211), was redistilled, the greater portion passing over at 193°–195°, without decomposition. Analysis of this fraction showed it to be pure nitroheptane.

0.1805 gram gave 16.1 cc. nitrogen at 746 mm. and 17°.

0.2253 gram gave 0.4761 gram CO_2, and 0.2043 gram H_2O.

	Calculated for $C_7H_{15}NO_2$.	Found.
C	57.93	57.65
H	10.34	10.04
N	9.65	9.87

Properties.—Nitroheptane is a light-yellow oil of peculiar pleasant odor. Boiling-point 193°–195° (uncorr.); specific gravity 0.9476 at 17°. It is insoluble in water, readily soluble in alcohol, ether, etc. It is very slowly soluble in aqueous solution of sodium or potassium hydroxide, readily soluble in their alcoholic solutions. It is not explosive.

The ready volatility of all these high-boiling nitroparaffins with a low-boiling solvent is remarkable. Heptane, boiling at 99°, carries over a noticeable quantity of nitroheptane when their mixture is distilled.

Sodium Nitroheptane, $C_7H_{14}NO_2Na$.—The action of metallic sodium on nitroheptane in a solution in petroleum ether apparently produced partial decomposition. The salt was therefore prepared by sodium ethylate in solution in petroleum ether, and after washing and drying was analyzed.

0.1650 gram gave 0.0700 gram Na_2SO_4.

	Calculated for $C_7H_{14}NO_2Na$.	Found.
Na	13.77	13.69

Properties.—Sodium nitroheptane is a light-yellow salt, readily soluble in water and in alcohol, insoluble in ether, petroleum ether, etc. While usually separating from all solvents as a gelatinous mass, it can with difficulty be crystallized from alcohol in fine, white needles. It blackens when heated, but is not explosive. Acids do not liberate the nitroparaffin.

With a solution of ferric chloride the characteristic intense red coloration results. The other metallic salts resemble those of nitrohexane, the mercuric derivative being yellow, the lead salt white, and the silver salt yellow, all flocculent precipitates.

Heptylamine, $C_7H_{15}NH_2$.—The reduction of nitroheptane to the amine proceeded smoothly on gently warming with iron filings and acetic acid. The heptylamine was liberated with

caustic soda, distilled in steam, the distillate extracted with ether, and the ether removed by distillation. Part of the residual heptylamine was dissolved in hydrochloric acid and platinic chloride added. Upon concentrating and cooling, the double salt crystallized out in fine needles, and was analyzed.

0.0137 gram gave, on ignition, 0.0041 gram Pt.

	Calculated for $(C_7H_{15}NH_3Cl)_2PtCl_4$.	Found.
Pt	29.82	29.92

The heptylamine gave the isonitril reaction, showing it to be primary. The action of nitrous acid on this amine gave what was apparently an alcohol, and this product, when Liebermann's reaction was applied, gave no evidence of a secondary amine.

Bromnitroheptane, $C_7H_{14}BrNO_2$.—V. Meyer and Tscherniak[1] have shown that if bromine-water is added to a solution of potassium nitroethane the following reaction takes place:

$$C_2H_4\begin{cases}K\\NO_2\end{cases} + Br_2 = C_2H_4\begin{cases}Br\\NO_2\end{cases} + KBr.$$

This bromnitroethane being a stronger acid than nitroethane liberates the latter from its salt, thus:

$$C_2H_4\begin{cases}K\\NO_2\end{cases} + C_2H_4\begin{cases}Br\\NO_2\end{cases} = C_2H_3\begin{cases}Br\\-K\\NO_2\end{cases} + C_2H_5NO_2.$$

The nitroethane thus liberated is not acted upon by the bromine, but the other product reacts as follows:

$$C_2H_3\begin{cases}Br\\-K\\NO_2\end{cases} + Br = C_2H_3\begin{cases}Br_2\\NO_2\end{cases} + KBr.$$

Hence the final product is a mixture of mono- and dibromnitroethane, and nitroethane.

When bromine water is added to an aqueous solution of sodium nitroheptane apparently analogous reactions result, for analysis shows the product to be a mixture. Tscher-

[1] Ber. d. chem. Ges., 7, 732.

niak,[1] however, has shown that if the alkaline salt of the nitroparaffin is added to an excess of bromine water, a practically pure monobromide results, and this method gives very satisfactory results with these higher nitroparaffins.

A few grams of nitroheptane were dissolved in a little alcoholic caustic soda, and the clear solution slowly added to a large excess of bromine water. A heavy oily bromide was precipitated. The solution was made alkaline with caustic soda, and the bromide extracted with ether. The ether was removed by gentle evaporation, and the residue dried in a vacuum desiccator and analyzed.

0.2256 gram, by ignition with lime, gave 0.1801 gram AgBr.

	Calculated for $C_7H_{14}BrNO_2$.	Found.
Br	35.71	34.02

The bromine water had been standing for some time and contained some hydrobromic acid which apparently liberated some nitroheptane, thus accounting for the somewhat low percentage of bromine.

Properties.—Bromnitroheptane is an almost colorless oil with a penetrating odor, affecting the eyes. It is insoluble in and heavier than water, soluble in alcohol, ether, etc., slowly soluble in concentrated aqueous solution of caustic soda; rather readily soluble in alcoholic caustic soda. It could not be solidified by a freezing-mixture of snow and salt. From the method of its preparation and its solubility in alkalies, its structure follows as $C_6H_{13}—C(H)(Br)(NO_2)$.

Heptylnitrolic Acid, $C_7H_{14}N_2O_3$.—A small quantity of nitroheptane was dissolved in alcoholic caustic potash, potassium nitrite added, the solution well cooled, and treated successively with excess of dilute sulphuric acid and of caustic potash. The red coloration due to the formation of the nitrolic acid appeared each time with excess of alkali. The process was twice repeated, then the slightly acid solution extracted with ether, and the ether removed from the extract by spon-

[1] Ann. Chem. (Liebig), 180, 126.

taneous evaporation. The residual nitrolic acid was a clear yellow liquid of sweet odor. It was converted into the fatty acid by digestion with dilute sulphuric acid[1] and the silver salt of the latter formed and analyzed.

0.0512 gram gave, on ignition, 0.0231 gram Ag.

	Calculated for $C_6H_{11}COOAg$.	Found.
Ag	45.57	45.30

Action of Hydrochloric Acid.—As a primary nitroparaffin, nitroheptane, when heated with concentrated hydrochloric acid, should yield heptoic acid and hydroxylamine, and this was found to be the case. About 5 grams of nitroheptane were heated in a sealed tube with 10 grams of concentrated hydrochloric acid for two hours at 125°. The reaction proceeded smoothly without the formation of a trace of resinous products. The tube was opened and the fat acid converted into the silver salt in the manner described under hexane. This silver salt was analyzed.

0.0256 gram gave, on ignition, 0.0116 gram Ag.

	Calculated for $C_6H_{13}COOAg$.	Found.
Ag	45.57	45.33

After removal of the fatty acid, the residual solution reduced Fehling's solution, showing the presence of hydroxylamine.

Dinitroheptane, $C_7H_{14}(NO_2)_2$.

The residue left after distilling off nitroheptane in steam from the mixed nitro-products is generally impure for the reason mentioned under dinitrohexane. Dinitroheptane is best obtained by the action of mixed sulphuric acid and nitric acid (of sp. gr. 1.42) on heptane when it usually partially separates as a middle layer, which may easily be purified by washing. Analysis of the compound thus obtained gave the following results:

0.1421 gram gave 18.4 cc. nitrogen at 738 mm. and 20°.

0.3317 gram gave 0.5407 gram CO_2, and 0.2011 gram H_2O.

[1] V. Meyer: Ann. Chem. (Liebig), **175**, 108.

	Calculated for $C_7H_{14}N_2O_4$.	Found.
C	44.21	44.45
H	7.37	7.08
N	14.74	14.37

Properties.—Dinitroheptane is a clear, yellow oil of pleasant ester-like odor, sparingly soluble in water, readily soluble in alcohol, ether, etc. It carbonizes on heating but is not explosive. It is very slowly soluble in aqueous solution of caustic soda, readily soluble in its alcoholic solution, with a red color.

Sodium Dinitroheptane, $C_7H_{13}(NO_2)_2Na$.—The sodium salt was precipitated by a solution of sodium ethylate in petroleum ether. The gelatinous mass thus obtained retained sodium ethylate with great persistency, and could not be obtained quite pure.

0.0941 gram gave 0.0371 gram Na_2SO_4.

	Calculated for $C_7H_{13}(NO_2)_2Na$.	Found.
Na	10.85	12.7

Properties.—Sodium dinitroheptane, when dry, is a yellow powder, turning red on exposure to light. It is readily soluble in water and alcohol, insoluble in ether, petroleum ether, etc. It could not be crystallized from any solvent. It always separates as a gelatinous mass. It blackens when heated, but is not explosive.

Addition of mercuric chloride to a solution of sodium dinitroheptane gives a yellow precipitate. The silver salt is yellow, rapidly darkening, and the lead salt is white. Ferric chloride in the cold gives immediately a red-brown precipitate.

Bromdinitroheptane, $C_7H_{13}Br(NO_2)_2$.—When a solution of sodium dinitroheptane was added to an excess of bromine water, a heavy oily bromide resulted. The solution was made alkaline with caustic soda and the bromide extracted with ether, the ether being then removed from the extract by gentle evaporation. The residual bromide was dried in a vacuum desiccator and analyzed.

0.2577 gram gave, by ignition with lime, 0.1790 gram AgBr.

	Calculated for $C_7H_{13}Br(NO_2)_2$.	Found.
Br	29.74	29.52

Properties.—Bromdinitroheptane is a light-yellow liquid of penetrating odor, affecting the eyes. Insoluble in, and heavier than, water. It is soluble in alcohol, ether, etc., insoluble in aqueous or alcoholic solution of caustic soda. Its structure must be represented by the formula,

$$C_6H_{13}—\overset{Br}{\overset{/}{C}}=(NO_2)_2.$$

Reduction of Dinitroheptane.—When dinitroheptane was reduced with tin and hydrochloric acid the products were ammonia, hydroxylamine, and a neutral product, probably an aldehyde. Hydroxylamine was shown to be present by the reducing action of the solution on Fehling's solution. The ammonia was distilled off in steam from the alkaline liquid and the chlorplatinate formed.

0.3735 gram gave 0.1617 gram Pt.

	Calculated for $(NH_4Cl)_2PtCl_4$.	Found.
Pt	43.92	43.30

Nitrooctane, $C_8H_{17}NO_2$.

The nitrooctane obtained by distilling the mixed nitrocompounds in steam (page 211) was dried and fractioned. It distilled chiefly between 206° and 210° with some decomposition.[1] This fraction was analyzed.

0.2523 gram gave 19.0 cc. nitrogen at 17° and 755 mm.

0.1334 gram gave 0.2968 gram CO_2, and 0.1242 gram H_2O.

	Calculated for $C_8H_{17}NO_2$.	Found.
C	60.37	60.64
H	10.69	10.35
N	8.83	8.64

Properties.—Nitrooctane is a light-yellow oil of pleasant ethereal odor. It boils at 206°–210° with some decomposition. Its specific gravity is 0.9346 at 20°. It is soluble in alcohol, ether, and other organic solvents, insoluble in water,

[1] Cf. Eichler: Ber. d. chem. Ges., 12, 1883.

very slowly soluble in aqueous solutions of caustic soda or caustic potash, readily soluble in their alcoholic solutions. Upon long standing the color turns to a red.

Sodium Nitrooctane, $C_8H_{16}NO_2Na$.—The sodium salt was prepared by means of a solution of sodium ethylate in petroleum ether in the manner previously described. The dried salt was analyzed.

0.1920 gram gave 0.0760 gram Na_2SO_4.

	Calculated for $C_8H_{16}NO_2Na$.	Found.
Na	12.70	12.76

Properties.—Sodium nitrooctane, when dry, is a yellow powder, readily soluble in water and in alcohol, insoluble in ether, petroleum ether, etc. It could not be crystallized, separating from all solvents as a gelatinous mass. Eichler[1] obtained the same result. It blackens when heated, but is not explosive. With ferric chloride the characteristic intense red coloration results. The other metallic derivatives resemble those of nitroheptane.

Octylamine, $C_8H_{17}NH_2$.—The reduction of nitrooctane to the amine was carried out with iron filings and dilute acetic acid. A primary amine resulted, giving the isonitril reaction. The chlorplatinate was formed by adding platinic chloride to the solution of the amine in hydrochloric acid. Upon concentrating and cooling, the chlorplatinate separated in fine yellow needles. Analysis of this double salt gave the following result:

0.1167 gram gave, by ignition, 0.0342 gram Pt.

	Calculated for $(C_8H_{17}NH_3Cl)_2PtCl_4$.	Found.
Pt	29.20	29.32

Bromnitrooctane, $C_8H_{16}BrNO_2$.—When sodium nitrooctane was dissolved in water and the solution treated with bromine water in excess, a heavy oil separated. This was washed with caustic soda, dried, and analyzed.

0.1224 gram gave, by ignition with lime, 0.0764 gram AgBr.

[1] *Loc. cit.*

	Calculated for $C_8H_{14}BrNO_2$.	Found.
Br	33.62	26.64

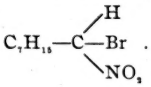
As shown before, under nitroheptane, this product was doubtless a mixture of nitrooctane, bromnitrooctane, and dibromnitrooctane.

When the solution of sodium nitrooctane was added to an excess of bromine water, however, the pure bromide was obtained. The heavy oil was washed with dilute caustic soda, extracted with ether, and the ether removed by evaporation. The residual bromide was dried in a vacuum desiccator and analyzed.

0.1730 gram gave, by ignition with lime, 0.1371 gram AgBr.

	Calculated for $C_8H_{14}BrNO_2$.	Found.
Br	33.62	33.53

Properties.—Bromnitrooctane is a yellow liquid, heavier than water. It is insoluble in water, soluble in alcohol, ether, etc., slowly soluble in concentrated aqueous solution of sodium or potassium hydroxides, readily soluble in their alcoholic solutions. It has a penetrating disagreeable odor, cannot be distilled without decomposition, and cannot be solidified by a freezing-mixture of snow and salt. Its structure follows from the method of its preparation and its properties as



Octylnitrolic Acid, $C_8H_{16}N_2O_3$.—About 10 grams of nitrooctane were dissolved in alcoholic caustic potash, potassium nitrite added, and the well-cooled solution slowly acidified with dilute sulphuric acid. With excess of caustic potash the red coloration due to a nitrolic acid appeared. The process was twice repeated, then the slightly acid solution was extracted with ether, and the ether removed from the extract by spontaneous evaporation, leaving the nitrolic acid as a light-yellow liquid of sweet odor.[1]

[1] Cf. Eichler: *Loc. cit.*

The nitrolic acid was converted into the fatty acid by digesting with dilute sulphuric acid. The fatty acid was extracted with ether, and the silver salt formed and analyzed.

0.1440 gram gave, on ignition, 0.0620 gram Ag.

	Calculated for $C_7H_{15}COOAg$.	Found.
Ag	43.07	43.10

Action of Hydrochloric Acid.—As a primary nitroparaffin, nitrooctane should, when heated with concentrated hydrochloric acid, yield octoic acid and hydroxylamine. About 5 grams of nitrooctane were heated in a sealed tube with 10 grams concentrated hydrochloric acid for two hours at 125°. Upon cooling and opening the tube no pressure was observed nor was there any resinous matter, indicative of secondary nitroparaffins. The fatty acid, present in large quantity, was converted into the silver salt in the way previously described, and the latter analyzed.

0.0412 gram gave, on ignition, 0.0180 gram Ag.

	Calculated for $C_7H_{15}COOAg$.	Found.
Ag	43.07	43.66

Dinitrooctane, $C_8H_{16}(NO_2)_2$.

The residue left after distilling off all nitrooctane in steam was found to be impure, as it is exceedingly difficult to drive over all nitrooctane without raising the temperature so high as partially to decompose the dinitrooctane. The latter is best obtained pure by the action of mixed sulphuric acid and nitric acid (sp. gr. 1.42) upon octane, when, on cooling, it partially separates as a middle layer.

Analysis of dinitrooctane obtained by the latter method gave the following results:

0.3964 gram gave 46.0 cc. nitrogen at 750 mm. and 15° C.

0.4884 gram gave 0.8469 gram CO_2, and 0.3559 gram H_2O.

	Calculated for $C_8H_{16}N_2O_4$.	Found.
C	47.06	47.27
H	7.84	8.08
N	13.73	13.63

Properties.—Dinitrooctane is a clear, yellow liquid which easily decomposes on heating. Its specific gravity is 1.0638 at 23°. It is soluble in alcohol, ether, etc., sparingly soluble in water. With alkalies either in aqueous or alcoholic solution it gives an intense red color. It could not be solidified by snow and salt.

Sodium Dinitrooctane, $C_8H_{15}(NO_2)_2Na$.—The sodium salt as obtained by precipitation with a solution of sodium ethylate in petroleum ether, retained sodium ethylate even after repeated washing with hot petroleum ether.

0.2432 gram gave 0.0816 gram Na_2SO_4.

	Calculated for $C_8H_{15}N_2O_4Na$.	Found.
Na	10.20	11.70

Properties.—Sodium dinitrooctane is a red salt, soluble in alcohol and water. It could not be crystallized. It resembled the corresponding salt of dinitroheptane.

Bromdinitrooctane.—When sodium dinitrooctane is added to an excess of bromine water, a heavy oily bromide separates which is insoluble in aqueous or alcoholic caustic soda. Its formula is doubtless $C_7H_{15}C\begin{matrix}Br\\(NO_2)_2\end{matrix}$, but it was not analyzed.

Reduction of Dinitrooctane.—When reduced with tin and hydrochloric acid, dinitrooctane yielded ammonia, hydroxylamine, and octoic acid as would be expected in the case of a primary dinitroparaffin.

The fatty acid formed was separated by distillation in steam, and the silver salt formed in the usual way and analyzed.

0.1360 gram gave 0.0785 gram AgCl.

	Calculated for $C_7H_{15}COOAg$.	Found.
Ag	43.07	43.38

The residual acid solution when made alkaline with caustic soda reduced Fehling's solution showing the presence of hydroxylamine. The ammonia was separated by distilling in steam, and converted into the chlorplatinate. Analysis of the latter gave the following result:

0.4885 gram gave 0.2137 gram Pt.

	Calculated for $(NH_4Cl)_2PtCl_4$.	Found.
Pt	43.92	43.75

Nitrononane, $C_9H_{19}NO_2$.

The distillate obtained from the mixed nitro-compounds by steam was redistilled in steam, the first portion of the distillate being rejected as possibly containin gnonane. Nitrononane completely decomposes when distilled under atmospheric pressure, but as above obtained it was a clear, light-yellow liquid, which analysis showed to be pure.

0.3164 gram gave 24.0 cc. nitrogen at 747 mm. and 17°.

0.2223 gram gave 0.5092 gram CO_2, and 0.2185 gram H_2O.

	Calculated for $C_9H_{19}NO_2$.	Found.
C	62.42	62.48
H	10.98	10.92
N	8.09	8.34

Properties.—Nitrononane is a light-yellow liquid of pleasant ester-like odor, boiling at 215°–218° with considerable decomposition, but volatile with steam. Its specific gravity is 0.9227 at 17°. Like the other nitroparaffins of high molecular weight it is insoluble in water, and practically insoluble in aqueous solution of caustic soda. It is readily soluble in alcohol, ether, etc., and in alcoholic caustic soda. It could not be solidified by a freezing-mixture of snow and salt, and was not explosive.

Sodium Nitrononane, $C_9H_{18}NO_2Na$.—The sodium salt was prepared by precipitation with sodium ethylate in petroleum ether solution. It retained sodium ethylate with persistency and was not obtained pure.

0.0765 gram gave 0.0332 gram Na_2SO_4.

	Calculated for $C_9H_{18}NO_2Na$.	Found.
Na	11.78	13.90

Properties.—The precipitated sodium salt as above obtained was a yellow, gelatinous mass which could not be crystallized. It was readily soluble in water and alcohol, gave the intense red coloration with ferric chloride, and blackened upon heating, but was not explosive.

Bromnitrononane, $C_9H_{18}BrNO_2$.—When bromine water was added to an aqueous solution of sodium nitrononane, apparently analogous reactions to those described by Meyer and Tscherniak[1] took place. A heavy oil was precipitated which was washed with caustic soda, dried, and analyzed.

0.2356 gram gave, by ignition with lime, 0.0785 gram AgBr.

	Calculated for $C_9H_{18}BrNO_2$.	Found.
Br	31.7	14.2

When the sodium salt was added to an excess of bromine water, however, the pure bromide was obtained. The oil thus formed was washed with caustic soda, dried in a vacuum-desiccator, and analyzed.

0.3064 gram gave 0.2270 gram AgBr.

	Calculated for $C_9H_{18}BrNO_2$.	Found.
Br	31.74	31.48

Properties.—Bromnitrononane is a clear, yellow liquid, slowly soluble in caustic potash. With sodium ethylate in solution in petroleum ether a sodium salt was precipitated. It has the characteristic, penetrating odor noticed in the case of the other bromides.

Nonylamine, $C_9H_{19}NH_2$.—A few grams of nitrononane were reduced to the amine by warming gently with iron filings and dilute acetic acid. The amine was liberated by caustic soda and distilled in steam. It gave the isonitril reaction, and with sodium nitroprusside and acetone it gave the deep-violet coloration recently shown by Rimini[2] to be characteristic only of primary amines.

The addition of platinic chloride to the solution of the amine in hydrochloric acid gave no precipitate, but upon concentrating and cooling, the double salt crystallized out in golden-yellow needles. These were dried and analyzed.

0.1472 gram gave, on ignition, 0.0417 gram Pt.

	Required for $(C_9H_{19}(NH_3Cl))_2PtCl_4$.	Found.
Pt	28.02	28.33

[1] *Loc. cit.*

[2] Chem. Centrbl., 1898, **2**, [2], 132.

Nonylnitrolic Acid, $C_9H_{18}N_2O_3$.—About 5 grams of nitrononane were dissolved in alcoholic caustic soda, sodium nitrite added, and the well-cooled solution slowly acidified with dilute sulphuric acid. Upon adding excess of alcoholic caustic soda again only a faint red color resulted. The process was twice repeated, then the faintly acid solution extracted with ether, and the ether removed from the extract by spontaneous evaporation.

By digesting with dilute sulphuric acid the yellow liquid left, it was shown to contain at least some nitrolic acid. A fatty acid was formed whose silver salt was analyzed.

0.1930 gram gave 0.0763 gram Ag.

	Calculated for $C_8H_{17}COOAg$.	Found.
Ag	40.75	39.55

Action of Hydrochloric Acid.—About 5 grams of nitrononane were heated in a sealed tube with 10 grams of concentrated hydrochloric acid for two hours at 120°. The reaction proceeded smoothly without the formation of resinous products, and the fatty acid was present in large quantity. The silver salt of the latter was analyzed.

0.2032 gram gave, on ignition, 0.0799 gram Ag.

	Calculated for $C_8H_{17}COOAg$.	Found.
Ag	40.75	39.32

After extracting the nonoic acid, the hydrochloric acid solution, when made alkaline with caustic soda, reduced Fehling's solution and gave off ammonia, thus showing the presence of hydroxylamine.

Dinitrononane, $C_9H_{18}(NO_2)_2$.—The residue left after distilling off nitrononane in steam from the mixed nitro-products of nonane had partially decomposed during distillation. Several nitrogen determinations gave a mean of 10.02 per cent in place of 12.84 per cent required by theory. But while the dinitroparaffin itself was impure, certain derivatives could be prepared from it in a pure state.

Sodium Dinitrononane, $C_9H_{17}N_2O_4Na$.—The sodium salt was

prepared by precipitation with sodium ethylate in solution in petroleum ether.

0.2198 gram gave 0.0680 gram Na_2SO_4.

	Calculated for $C_9H_{17}N_3O_4Na$.	Found.
Na	9.59	10.05

Properties.—Sodium dinitrononane resembled the corresponding derivative of dinitrooctane. It was yellowish-red, soluble in water and alcohol, and was deposited from either solvent as a gelatinous mass that could not be crystallized.

Bromdinitrononane, $C_9H_{16}BrN_3O_4$.—When a solution of sodium dinitrononane was added to an excess of bromine water, a heavy oily bromide was precipitated. The solution was made alkaline with caustic soda, and the bromide extracted with ether. The ether was removed by gentle evaporation.

0.3123 gram, by ignition with lime, gave 0.1936 gram AgBr.

	Calculated for $C_9H_{17}BrN_3O_4$.	Found.
Br	26.9	26.6

Properties.—Bromdinitrononane is a heavy, yellow liquid, insoluble in water, soluble in alcohol, ether, etc., insoluble in concentrated aqueous or alcoholic caustic soda. It could not be solidified by snow and salt.

Reduction of Dinitrononane.—A small quantity of dinitrononane was reduced with iron filings and acetic acid, the mixture being gently warmed. The acid solution was partially neutralized with caustic soda, then extracted with ether, and the ether evaporated from the extract. The residual fatty acid was boiled with calcium carbonate, and filtered. The silver salt was precipitated from the filtrate, washed, dried, and analyzed.

0.0778 gram gave 0.0320 gram Ag.

	Calculated for $C_8H_{17}COOAg$.	Found.
Ag	40.75	41.13

The other product of the reaction was ammonia.

Nitrodecane, $C_{10}H_{21}NO_2$.

The distillate obtained by steam from the mixed nitro-products of decane was again distilled in steam, dried, and analyzed.

0.1404 gram gave 0.3313 gram CO_2, and 0.1399 gram H_2O.

	Calculated for $C_{10}H_{21}NO_2$.	Found.
C	64.17	64.35
H	11.23	11.07

Properties.—Nitrodecane is a clear, yellow liquid with the peculiar sweet odor characteristic of these higher nitroparaffins. Its specific gravity is 0.9105 at 15°.[1] It cannot be distilled without decomposition, but is volatile with steam. It is readily miscible with alcohol, ether, etc., soluble in alcoholic caustic potash. The nitrolic-acid test resulted in an orange-red coloration, and the sodium salt gave a brown precipitate with ferric chloride.

Nitrohendecane, $C_{11}H_{23}NO_2$.

Nitrohendecane was separated from the dinitroparaffin by two distillations in steam. Analysis showed it to be pure.

0.1731 gram gave 0.4200 gram CO_2, and 0.1776 gram H_2O.

	Calculated for $C_{11}H_{23}NO_2$.	Found.
C	65.67	65.42
H	11.44	11.36

Properties.—The nitrohendecane is a clear, yellow liquid of specific gravity 0.9001 at 15°. It cannot be distilled without decomposition but is volatile with steam. It is readily miscible with alcohol and ether, insoluble in water. The nitrolic-acid test resulted in an orange-yellow coloration.

Nitrododecane, $C_{12}H_{25}NO_2$.

The nitrododecane obtained by two distillations in steam still contained traces of the free hydrocarbon, analyses showing both carbon and hydrogen too high. The quantity at hand was too small to admit of purification. The nitrododec-

[1] The specific gravity determination of this and the two higher nitroparaffins were necessarily carried out with small quantities of material. But it is believed that the figures given are fairly accurate.

ane resembled the preceding nitroparaffin, the nitrolic-acid test resulting in a yellow coloration.

An investigation of certain other derivatives and reactions of these higher nitroparaffins is now in progress.

LAFAYETTE, IND., Dec., 1898.

THE ACTION OF ETHYLIC OXALATE ON CAMPHOR. (IV).

BY J. BISHOP TINGLE AND ALFRED TINGLE.

Theoretical.

In the previous papers on this subject[1] Bishop Tingle has described the method employed for the preparation of camphoroxalic acid. We have now succeeded in improving and simplifying the process by hydrolyzing the mixture of borneol, camphor, and ethylic camphoroxalate together in one operation, so that the preparation and purification of the compound need only occupy a few hours distributed over three days.

According to the experimental conditions, three compounds are formed by the interaction of aniline and camphoroxalic acid. For the sake of convenience we will describe the preparation and chief properties of them all before discussing their constitution. When aniline (2 mols.) and camphoroxalic acid (1 mol.) are heated together at 130° a compound, $C_{17}H_{21}NO$, is formed which crystallizes in colorless, rhombic plates, and occasionally in slender, hair-like needles, upwards of an inch in length. It is readily soluble in benzene or ethylic acetate, but only sparingly so in light petroleum, and melts at 166°. It does not react with ferric chloride; bromine causes the production of a hydrobromide, whilst hydroaurochloric acid and hydroplatinochloric acid yield the corresponding salts, of which the former is very unstable. Prolonged boiling with concentrated alkali is without appreciable effect on the base. The second compound is formed by mixing concentrated benzene solutions of aniline (2 mols.) and camphoroxalic acid (1 mol.), and warming the liquid for a few moments on the water-bath. The compound crystallizes from

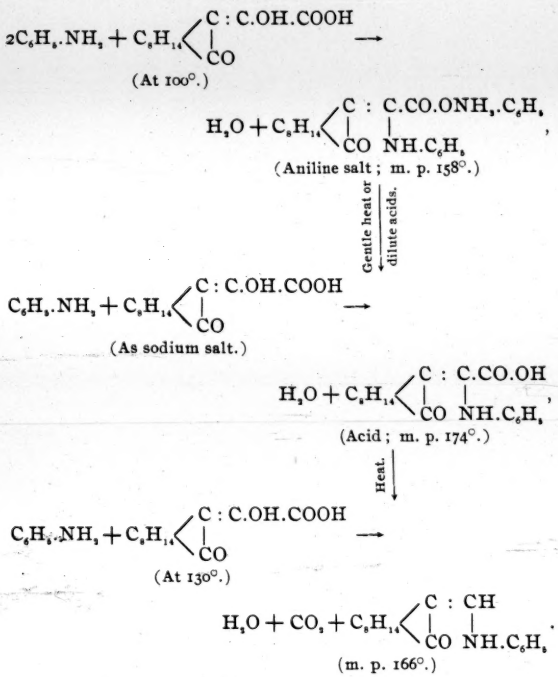
[1] This JOURNAL, **20**, 318 (1898); *Ibid.*, **19**, 393 (1897); J. Chem. Soc., **57**, 652 (1890).

a mixture of benzene and light petroleum in small, colorless needles, which melt and decompose at 158°. The substance is an aniline salt and has the formula $C_{24}H_{28}N_2O_5$. When slowly heated below its melting-point, it gives up aniline and yields the third compound described below. If quickly heated above its melting-point, it yields aniline, carbon dioxide, and the substance (m. p. 166°) already described. In the absence of moisture and acid vapors this aniline salt is stable, but it is slowly hydrolyzed on warming with water or alcohol; alkalies decompose it much more rapidly, and in two stages: in the first stage the alkali salt of the corresponding acid is produced, with liberation of aniline; in the second stage this salt is broken down as described later.

By the action of dilute (1 : 6) sulphuric acid, or hydrochloric acid, at the ordinary temperature the aniline salt suffers immediate decomposition, aniline is eliminated, and a yellow acid, $C_{18}H_{21}NO_4$, is formed which is insoluble in water. It is deposited from a mixture of benzene and light petroleum in bright yellow needles, and melts and decomposes at 174°.

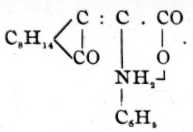
The third compound which we have obtained from aniline and camphoroxalic acid is identical with the foregoing substance, and is also prepared by boiling aniline with sodium camphoroxalate, in equimolecular proportion, in dilute alcoholic solution. The compound has well-developed acidic properties, and liberates carbonic anhydride from an aqueous solution of sodium carbonate; the sodium salt is practically colorless. Prolonged boiling with concentrated alcoholic potash or soda causes a slow decomposition of the compound into aniline and camphoroxalic acid. When heated above its melting-point alone, or at 140° in the presence of ethylaniline, carbonic anhydride is evolved, and the compound first described (m. p. 166°) is produced.

For convenience we give a diagrammatic representation of the modes of formation and interrelationship of the foregoing compounds and of the formulæ which we assign to them:

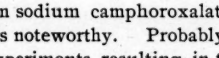

2C6H5.NH2 + C8H14 C : C.OH.COOH / CO
(At 100°.)
H2O + C8H14 C : C.CO.ONH3.C6H5 / CO NH.C6H5
(Aniline salt; m. p. 158°.)
Gentle heat or dilute acids.
C6H5.NH2 + C8H14 C : C.OH.COOH / CO
(As sodium salt.)
H2O + C8H14 C : C.CO.OH / CO NH.C6H5
(Acid; m. p. 174°.)
Heat.
C6H5.NH2 + C8H14 C : C.OH.COOH / CO
(At 130°.)
H2O + CO2 + C8H14 C : CH / CO NH.C6H5
(m. p. 166°.)

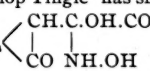
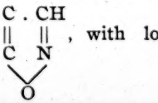
Various names suggest themselves for the compounds; we believe the simplest plan to adopt is to regard them as being derived from the complex $C_8H_{14}\begin{cases} C : CH_2 \\ | \\ CO \end{cases}$ for which the term camphoformene may be employed. It is self-explanatory, and indicates the presence of the double linkage. The first of the above compounds is then aniline phenylcamphoformeneamine carboxylate; the second, phenylcamphoformeneaminecarboxylic acid; whilst the third is phenylcam-

phoformeneamine. The pronounced yellow color of the carboxylic acid, and its absence from the aniline and sodium salts makes it probable that there is a more intimate linkage in the first than in the others, so that the free acid should possibly be represented by the "betaïne" formula,



We have not observed any similar recorded instance of the action of aniline on an unsaturated hydroxy acid, and we believe that the formation of phenylcamphoformeneaminecarboxylic acid from sodium camphoroxalate under the conditions described is noteworthy. Probably the first product in this, as in the experiments resulting in the formation of the other compounds, is a purely additive one; *viz.*,

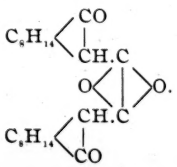


which must be highly unstable, as we have hitherto failed to isolate it. By loss of the elements of water it then passes into the unsaturated carboxylic acid. This view of the reaction brings it into harmony with that of hydroxylamine and sodium camphoroxalate, which, as Bishop Tingle[1] has shown, yield the additive compound,  . This substance is quite stable, and can, without difficulty, be converted into the isoxazole,  , with loss of 2 molecules of water, a reaction analogous, to some extent, with that leading to the formation of the above phenylcamphoformeneamine. On account of this analogy the possible alterna-

[1] This JOURNAL, 19, 393 (1897).

tive formula $C_8H_{14}<\begin{matrix}C(=CH.CO.OH)\\CO\,N.C_8H_8\end{matrix}$ for the carboxylic acid suggests itself. At present we believe that the properties of the compound and the conditions under which it is formed are not such as to justify the assumption of the production of a closed chain, even apart from the question of analogy. Subsequently to Bishop Tingle's work just referred to C. Harries[1] and his colleagues showed that hydroxylamine also forms additive compounds with various unsaturated ketones such as phorone.

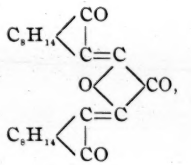
In addition to acetylcamphoroxalic acid (m. p. 133°.5–134°.5), Bishop Tingle[2] has described two other compounds formed by the action of acetic anhydride on camphoroxalic acid, which melt at 190°–191° and 242°–242°.5, respectively. We have prepared the former in somewhat larger quantity by boiling camphoroxalic acid with benzoyl chloride. The compound crystallizes from a mixture of benzene and light petroleum in minute colorless needles; it is not changed by boiling with sodium hydrate solution, nor does it combine with bromine in chloroform solution; hydroxylamine is also without action on the substance. Analyses and molecular weight determinations by the cryoscopic method lead to the formula $C_{22}H_{30}O_4$. The compound is evidently not an anhydride as was at first suggested; we believe that it may be best represented, at least provisionally, by the formula



The high-melting compound referred to above has also been obtained in somewhat larger quantity by boiling acetic anhydride with camphoroxalic acid. Its production appears to be dependent on the strict purity of the anhydride and the dura-

[1] Ber. d. chem. Ges., 30, 231 et seq. [2] This JOURNAL, 20, 324 (1898).

tion of the heating. With inferior specimens of anhydride none of the compound is formed; boiling during periods much less than two hours gives rise to uncrystallizable resinous substances, whilst camphor is the chief product if the heating is prolonged much beyond that time. These observations explain the difficulties previously encountered in the preparation of this body. The compound does not react with alcohol and ferric chloride, nor with bromine in chloroform solution; with aqueous sodium hydrate a portion dissolves and the remainder acquires a yellow color. Analysis leads to the empirical formula $C_{23}H_{28}O_4$; graphically we may represent the compound as



which is in harmony with the little we know of it.

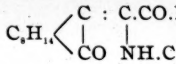
Professor Carter has communicated to us the result of an additional experiment on the physiological action of camphoroxalic acid. He finds that when injected intravenously, to the extent of 0.241 gram per kilo of body weight, it is practically without effect. The results previously obtained[1] therefore require correction.

The good yield of ethylic camphoroxalate obtained from the acid by E. Fischer's method led us to determine the effect of the duration of the time of heating. We find that the yield is practically the same whether the acid is boiled during seven and three-fourths hours or during thirteen hours. In Fischer and Speier's experiments[2] absolute alcohol was exclusively employed. As this is not always readily available, it occurred to us to try the effect of 90 per cent. alcohol, together with a larger quantity of sulphuric acid (7 per cent by volume). The yield, after boiling during eleven and a half hours, was 93.3 per cent of the camphoroxalic acid employed. We hope that

[1] This JOURNAL, **20**, 342 (1898). [2] Ber. d. chem. Ges., **28**, 3252.

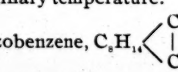
this modification of the original method may find a useful and wider application.

When ethylic camphoroxalate is heated at 130° with aniline, water and alcohol are eliminated and phenylcamphoformeneaminecarboxylic anilide,



is produced. It crystallizes from a mixture of benzene and light petroleum in small, colorless needles, melting at 193°. The compound is not changed by bromine in chloroform solution, nor by prolonged boiling with alcoholic or aqueous soda. Treatment with sulphuric acid readily gives rise to resinous products. An unstable platinochloride appears to be formed, but auric chloride in dilute hydrochloric acid solution quickly undergoes reduction.

We desire to take this opportunity of correcting an error in Bishop Tingle's first paper on this subject[1] in which it is stated that aniline and ethylic camphoroxalate yield oxanilide. At that time pure ethylic oxalate had not been prepared, and the mistake arose from the use of the crude compound containing ethylic oxalate in much larger proportion than was suspected. Unfortunately the erroneous statement has been copied into Morley & Muir's edition of "Watts' Dictionary of Chemistry."

In continuation of experiments previously recorded,[2] we attempted to isolate the oxidation-product of ethylic camphoroxalate phenylhydrazide. Mercuric oxide does not appear to be a suitable reagent to employ for its production, but good results were obtained by the use of hydrogen peroxide in ethereal solution at the ordinary temperature. The resulting ethylic camphor oxalate azobenzene,  , crystallizes from a mixture of ethylic acetate and light petroleum in red needles, melting at 210°. It is much more readily soluble in ether than the phenylhydrazide, and is only slowly attacked by glacial acetic acid.

[1] J. Chem. Soc., **57**, 655 (1890). [2] This JOURNAL, **20**, 338 (1898).

An unsuccessful attempt was made to prepare isoamylic camphoroxalate by boiling the acid with excess of isoamylic alcohol containing 4.57 per cent of hydrogen chloride. The product ultimately obtained could not be induced to crystallize, owing to the presence of impurities of high boiling-point. These were probably chlorine derivatives, originating from the action of hydrogen chloride on the isoamylic alcohol. It would be interesting to investigate whether any modification of Fischer's method of etherification could be devised which would permit its use for the preparation of the ethereal salts of the higher aliphatic alcohols.

In a discussion of the formation of camphoroxalic acid[1] an explanation was suggested based on Claisen's theory of the interaction of ketones, $R.CO.CH_2X$, and ethereal salts. The hypothesis given involves the successive production of the hypothetical compounds $NaO.C(OR)_2.C(OR)_2.ONa$ and $C_8H_{14}<\begin{matrix}CO\\|\\C:C.ONa.C(OR)_2.ONa\end{matrix}$ before the treatment with water, and of the compound $C_8H_{14}<\begin{matrix}CO\\|\\C:C.ONa.CO.ONa\end{matrix}$ afterwards ($R=C_2H_5$ or $C_{10}H_{18}$). Should this explanation be valid, then, apart from possible stereoisomers, only one acid can be produced from camphor and ethylic oxalate on account of the molecular symmetry of the latter, but if an unsymmetrical dibasic acid were employed two structurally different acids might be obtained according to which of the original carbethoxyl groups reacted with the camphor, thus:

The first additive compound $NaO.\overset{1}{C}(OR)_2\cdots\overset{2}{C}(OR)_2.ONa$, would become successively

(*A*) $NaO\overset{1}{C}:CR''\cdots\overset{2}{C}(OR)_2.ONa$ or

$NaO.\overset{1}{C}(OR)_2\cdots\overset{2}{C}.ONa:CR''$,

(*B*) $NaO\overset{1}{C}:CR''\cdots\overset{2}{C}<\begin{matrix}O\\\\ONa\end{matrix}$ or $NaO.\overset{1}{C}O\cdots\overset{2}{C}.ONa:CR''$,

(*C*) $HO.\overset{1}{C}:CR''\cdots\overset{2}{C}O.OH$ or $HO.\overset{1}{C}O\cdots\overset{2}{C}.OH:CR''$,

[1] This JOURNAL, **19**, 407 (1897).

($R=C_2H_5$ or $C_{10}H_{15}$; $R''=C_8H_{14}\langle\begin{smallmatrix}CO\\ \diagup\quad\diagdown\end{smallmatrix}\rangle$). The original carbethoxyl carbon atoms have been numbered 1 and 2 for the sake of clearness. Pyrotartaric acid, $CH_3.\underset{\displaystyle COOH}{\underset{|}{CH}}.CH_2.COOH$, is perhaps the simplest acid fulfilling the conditions necessary to test this hypothesis, and our first experiments on the lines indicated were made with it. Diethylic pyrotartrate is readily prepared by Fischer's method, and the yield is very good.

Sodium wire only dissolves slowly in a light petroleum solution of camphor and ethylic pyrotartrate. The product, treated in the manner previously described for camphor and ethylic oxalate, yields a condensation-compound which gives a red coloration with ferric chloride and alcohol. Attempts to hydrolyze it were unsuccessful; the acid is evidently much less stable toward alkalies than camphoroxalic acid, and under the conditions we employed, was resolved into its constituents. The yield of condensation-product was somewhat small, and we endeavored to increase it by varying the experimental conditions, but, hitherto, without success.

In the hope that a more favorable result might be obtained with oxalacetic acid, which is also an unsymmetrical dibasic acid, we investigated the interaction of camphor and ethylic oxalacetate in presence of sodium. The resulting product is a syrup, which, in aqueous solution, acquires a blue-purple color on the addition of dilute mineral acids in not too great excess. In ethereal solution the compound is yellowish-brown. With aqueous alkali a deep-red coloration is produced which changes to the blue on the addition of a little acid, but disappears when a large excess is added. An attempt to obtain a crystalline acid by hydrolyzing the above syrup was uusuccessful, as was also an effort to purify it by means of the barium salt. The compound has well-marked acidic properties and liberates carbon dioxide from aqueous alkali carbonates. No substance corresponding to camphoroxalic acid could be isolated, and, in view of the investigations of Claisen alone,[1] and in conjunction with Hare,[2] and

[1] Ber. d. chem. Ges., **24**, 130. [2] *Ibid.*, **24**, 120.

also that of Ruhemann and Hemmy,[1] it appears probable that the above compound is a condensation-product of ethylic oxalacetate resembling some of those described by these workers.

We desire also to record the results of some preliminary experiments which we have made on the condensation of ethylic oxalate and thymol, in presence of sodium. The resulting compound has hitherto only been obtained as an oil. It gives a dark-red coloration with ferric chloride and alcohol, but is apparently not very stable towards alkalies. We have obtained, in addition, some evidence of the simultaneous formation of a substance analogous to camphoroxalic acid. Should further investigation confirm these results proof would be afforded of the reaction of thymol in its "secondary" or tautomeric form, $(CH_3)_2CH.C\begin{cases}CO.CH_2\\ CH.CH\end{cases}C.CH_2$, and an interesting field of research amongst other phenols would be opened up.

EXPERIMENTAL.

Preparation of Camphoroxalic Acid.

The method for the preparation of camphoroxalic acid, described in the previous papers on this subject, has been considerably simplified. The product obtained by the action of sodium on camphor and ethylic oxalate (8 or 12 portions) is well shaken with water, the light petroleum solution removed, dried, and the solvent distilled off. The aqueous extract is acidified with dilute sulphuric acid and extracted four times with ether. This ethereal solution is dried, the ether removed, and the residue combined with that from the light petroleum extract. The semi-solid mass is mixed with about 2 liters of water, together with a considerable excess of solid sodium hydrate, and boiled during half an hour; the product is cooled, filtered, and the solid residue repeatedly boiled in the same manner with sodium hydrate solution until a portion of the clear liquid, after acidifying with hydrochloric acid, fails to give a coloration with ferric chloride solution and alcohol. As a rule, about six extractions are required to remove

[1] J. Chem. Soc., 71, 334 (1897).

all the camphoroxalic acid. The combined alkaline liquors are acidified with dilute sulphuric acid and allowed to remain for a short time; the greater portion of the camphoroxalic acid is obtained in crystals, and the remainder by extracting the filtrate once with ether.

Action of Aniline on Camphoroxalic Acid.

(1) *Preparation of Phenylcamphoformeneamine.*—Camphoroxalic acid (13.2 grams) is mixed with an equimolecular proportion of aniline (6 grams) and heated in a paraffin-bath at 130° for thirty minutes. The reaction proceeds quietly and water is evolved in considerable quantity. The product readily crystallizes on the addition of a solvent, and the yield of crude substance is 10.7 grams. The amine easily dissolves in alcohol, benzene, and ethylic acetate, but only sparingly in light petroleum; it crystallizes in colorless rhombic plates, and occasionally forms very characteristic hair-like needles exceeding an inch in length. Difficulty was experienced in the analysis, due probably to traces of gummy matter which appear to be formed during each recrystallization. For the analysis given below, the specimen was recrystallized six times from ethylic acetate and light petroleum, and benzene and light petroleum, then finally from alcohol, when it melted at 166°. The results of the analyses are given below:

I. 0.2800 gram substance gave 0.2112 gram H_2O, and 0.8158 gram CO_2.

II. 0.2679 gram substance gave 13.6 cc. nitrogen at 25°.5 and 743 mm.

	Calculated for $C_8H_{14}\begin{cases} C:CH \\ \vert \quad \vert \\ CO\ NH.C_6H_5 \end{cases}$	Found. I.	Found. II.
C	80.00	79.46	....
H	8.23	8.38	....
N	5.49	....	5.51

The compound gives no coloration, in alcoholic solution, with aqueous ferric chloride. When treated with bromine, in benzene solution, decolorization takes place, hydrogen bromide is evolved, and a precipitate is formed. This substance is colorless, and is probably a hydrobromide; it melts at about

216° and previously darkens. With auric chloride and hydrochloric acid, in alcoholic solution, phenylcamphoformeneamine yields a crystalline compound which is unstable and speedily decomposes, a black amorphous deposit being formed which appears to contain metallic gold. Platinic chloride, under similar conditions, gives a platinochloride, $(C_{17}H_{21}NO)_2 . H_2PtCl_6$, which crystallizes in dark, orange-colored needles, and is readily soluble in alcohol, but insoluble in water. The base is not affected by sodium hydrate; when boiled for two hours with a large excess of concentrated aqueous soda it is not perceptibly changed. Proof of the constitution of phenylcamphoformeneamine is furnished by its production from the carboxylic acid, when this is heated above its melting-point either alone or in presence of ethylaniline.

(2) *Preparation of Aniline Phenylcamphoformeneaminecarboxylate.*—Camphoroxalic acid (1 mol.) and aniline (2 mols.) are separately dissolved in the smallest requisite quantity of warm benzene, the solutions mixed and gently heated on the water-bath. The mixture almost solidifies in the course of a few minutes. It is allowed to cool and the mother-liquor drained off. The compound crystallizes from benzene, on the addition of light petroleum, in very small colorless needles melting at 158° with decomposition.

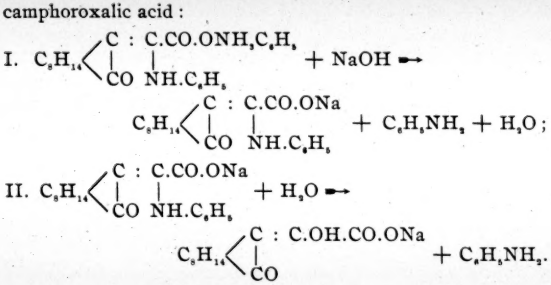
I. 0.2161 gram substance gave 0.1428 gram H_2O, and 0.5798 gram CO_2.

II. 0.1776 gram substance gave 11.7 cc. nitrogen at 19° and 755 mm.

	Calculated for $C_8H_{14}\langle \overset{C : C.CO.ONH_3.C_6H_5}{\underset{CO\ NH.C_6H_5}{|}} \rangle$.	Found. I.	Found. II.
C	73.46	73.17	....
H	7.14	7.34	....
N	7.14	....	7.50

The compound is highly unstable in presence of even traces of acid vapors (cf. following reaction), but in an atmosphere free from these it may be retained without decomposition. It is slowly hydrolyzed by water, or even dilute alcohol. With aqueous soda or alcoholic potash decomposition is rapid and takes place in two stages: Aniline and the alkali salt of

phenylcamphoformeneaminecarboxylic acid are first formed, and the latter then slowly decomposes under the continued action of the heated alkali into aniline, and the alkali salt of camphoroxalic acid :



The camphoroxalic acid is recognized by the ferric chloride test, the aniline by the isonitril reaction :

When slowly heated alone, below its melting-point, the compound yields aniline, and phenylcamphoformeneaminecarboxylic acid, which at higher temperatures is resolved into carbonic anhydride and phenylcamphoformeneamine.

Preparation of Phenylcamphoformeneaminecarboxylic Acid.— Aniline phenylcamphoformeneaminecarboxylate is triturated with dilute (1 : 6) sulphuric acid, or dilute hydrochloric acid at the ordinary temperature. The salt, without dissolving, immediately acquires a bright-yellow color. The excess of acid, which contains aniline sulphate or hydrochloride, is removed, the residue washed once or twice with cold water, dried, and recrystallized from benzene with the addition of light petroleum. It is readily soluble in the former, almost insoluble in the latter, and is deposited in bright-yellow needles, which resemble iodoform in color, and melt and decompose at 174° when quickly heated. The yield is quantitative.

The compound is also formed by the action of aniline on sodium camphoroxalate. Camphoroxalic acid (2.2 grams = 1 mol.) is dissolved in the smallest quantity of alcohol, water and sodium hydrogen carbonate are added until the solution is clear and has a faintly alkaline reaction. It is now mixed

with aniline (1 gram = 1 mol.), together with more alcohol, if necessary, and the clear liquid allowed to remain during twenty-four hours at the ordinary temperature, and then boiled during fourteen hours in a reflux apparatus. The product is poured into excess of dilute sulphuric acid, extracted with ether, the ethereal solution dried, the ether removed, and the residue purified in the manner described above. The yield is good. Apart from the analyses, the identity of the compounds obtained by both methods of preparation was established by simultaneous melting-point determinations, and also by the fact that a mixture of both in equal proportion melted at the same temperature as either separately.

I. 0.2690 gram substance gave 0.1760 gram H_2O, and 0.7080 gram CO_2.

II. 0.2131 gram substance gave 0.1430 gram H_2O, and 0.5603 gram CO_2.

III. 0.1882 gram substance gave 8.4 cc. nitrogen at 29° and 742 mm.

IV. 0.1500 gram substance gave 6.6 cc. nitrogen at 29° and 737 mm.

	Calculated for $C_8H_{14}\langle^{C:C.COOH}_{CO\ NH.C_6H_5}$	Found. I.	II.	III.	IV.
C	72.24	71.78	71.70	....	....
H	7.02	7.26	7.45	....	....
N	4.68	....	....	4.74	4.65

Analysis I. was made with a preparation from aniline phenylcamphoformeneaminecarboxylate; for the remainder specimens obtained from sodium camphoroxalate were employed.

Phenylcamphoformeneaminecarboxylic acid readily dissolves in a solution of sodium carbonate, carbonic anhydride being liberated, and also in aqueous sodium hydrate, the solutions being almost colorless. Prolonged boiling with a considerable excess of concentrated aqueous sodium hydrate, in presence of a little alcohol, causes a slow decomposition; aniline is evolved, and camphoroxalic acid is produced, but no

oxalic acid. When heated above its melting-point, or at 140° in presence of ethylaniline, phenylcamphoformeneaminecarboxylic acid yields carbonic anhydride and phenylcamphoformeneamine.

Action of Benzoyl Chloride on Camphoroxalic Acid.

The formation of a compound (m. p. 190°–191°), by the action of acetic anhydride, or of benzoyl chloride, on camphoroxalic acid, has been previously described by Bishop Tingle.[1] It is most readily obtained by boiling the acid (4.4 grams = 1 mol.) with the chloride (4 grams = 1.5 mols.) during fifteen minutes. The product is poured into a solution of sodium hydrogen carbonate; the black pasty mass which separates is dried on a porous plate and recrystallized several times from a mixture of benzene and light petroleum. The yield is not very large. The substance is deposited in minute colorless needles and is not changed by boiling with a solution of sodium hydrate, nor by heating with hydroxylamine in large excess in presence of alkali; bromine, in warm chloroform solution, is also without action on the compound.

I. 0.2520 gram substance gave 0.1844 gram H_2O, and 0.6788 gram CO_2.

II. 0.2504 gram substance gave 0.1810 gram H_2O, and 0.6750 gram CO_2.

	Calculated for $C_{23}H_{30}O_4$. Mol. wt. = 358.	Found. I.	II.
C	73.74	73.46	73.51
H	8.37	8.13	8.03

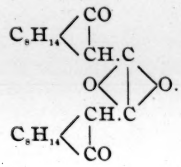
Molecular weight determinations:

Solvent, nitrobenzene. $\iota = 7100$.

Weight of solvent. Grams.	Weight of substance in solution. Gram.	Δ.	m.
13.7802	0.0605	0.15°	207.8
13.7802	0.3137	0.51°	316.9
13.7802	0.7007	1.09°	331.1

We suggest for this compound the formula

[1] This JOURNAL, **20**, 324, 328 (1898).



Action of Acetic Anhydride on Camphoroxalic Acid.

Three compounds have been previously obtained[1] by the action of acetic anhydride on camphoroxalic acid. They melted at 118°, 191°, and 242°, respectively, and were all formed in small quantity. The first was shown to be acetyl-camphoroxalic acid; the second, also formed by the action of benzoyl chloride on camphoroxalic acid, is described above. We have obtained the third compound in slightly larger quantity, but on account of the poor yield it has not been possible to pursue its investigation to a satisfactory conclusion. It is obtained by boiling camphoroxalic acid (2.2 grams) with acetic anhydride (5.1 grams) during two hours. The product is poured into a solution of sodium hydrogen carbonate. Should it become pasty after remaining in contact with the alkaline liquid for some time, it is removed and dried on a porous plate, otherwise it is extracted by means of ether. It is recrystallized several times from mixtures of benzene or ethylic acetate and light petroleum. In the first two it dissolves very readily but in the last it is practically insoluble. The compound is deposited in small, slender, colorless needles; it gives no coloration with ferric chloride and alcohol; with aqueous sodium hydrate a portion dissolves, and the remainder becomes yellow; bromine, in chloroform solution, is without action on the substance either at the ordinary temperature or when warmed on the water-bath. The yield is only 1.5 grams from 11 grams of acid, and even this is greatly diminished unless the above conditions are adhered to. Resinous bodies only are obtained if the time of heating is from ten to twenty minutes, whilst camphor, which, in varying proportion, always accompanies the crude substance,

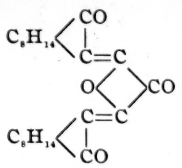
[1] *Loc. cit.*

becomes the chief product when the heating is extended beyond two hours. The purity of the acetic anhydride is also a factor of great importance. At the commencement of the reaction a considerable evolution of carbon dioxide takes place. These observations explain the difficulties previously encountered in connection with the preparation of this compound.

0.2270 gram substance gave 0.1546 gram H_2O, and 0.6216 gram CO_2.

	Calculated for $C_{22}H_{32}O_4$.	Found.
C	75.00	74.68
H	7.60	7.56

A molecular-weight determination by the cryoscopic method failed to give a satisfactory result. It is evident from the foregoing description that the compound originates in consequence of some deep-seated molecular change. Our knowledge of the nature of this and of the reactions of the substance are inadequate for the deduction of its formula with any approach to certainty. We think, however, that the expression



may serve as a first step in this direction, and we believe it to be in harmony with the results of our observations.

Physiological Action of Sodium Camphoroxalate.

An additional experiment[1] on the physiological action of sodium camphoroxalate has been made with the following results: The dog employed weighed 12.023 kilos and had been used for another experiment which had produced no effect on his circulation. A 2 per cent solution of the sodium camphoroxalate in normal saline solution was introduced into the jugular vein.

[1] We are indebted for it to Prof. Carter of the University of Texas.

Time. P. M.	Blood pressure in mm. mercury.	Pulse in ten seconds.	Dose. cc.	Remarks.
12.50	128	15		
12.50.25			5	
12.50.50	132		5	
12.51.10	132		5	
12.51.20	133		5	
12.52.00	132	15		Struggling respiration throughout entire experiment prevented satisfactory counting of the pulse.
12.53.00	131			
12.54.00	133			
12.54.20			10	
12.55.10	132		10	
12.56.00	140	17	20	
12.56.30	140			
12.56.50	140	22	20	
12.57.00	142			
12.58.00	142	19		
12.58.15			20	
12.59.00	130	17	5	
12.59.40	142			
1.00.00	118			
1.02.30	110	15		
1.02.40			10	These doses were made up from a preparation of sodium camphoroxalate different from that employed in the earlier part of the experiment.
1.03.00	106	15		
1.03.10			10	
1.03.35	120		10	
1.04.00	118	18		
1.04.40	110	17	10	
1.05.00	110			
1.08.00				Killed by chloroform.

These results show that sodium camphoroxalate, even to the extent of 0.241 gram per kilo of body weight, has practically no physiological effect. Death in the former experiments[1] was not due to this, but arose from the escape into the jugular of the solution of magnesium sulphate which was employed to fill the cannula.

Etherification of Camphoroxalic Acid.

Two experiments were made in the manner previously de-

[1] This JOURNAL, **20**, 342 (1898).

scribed[1] to determine the influence of the duration of heating on the yield of ethylic camphoroxalate. The acid (44.8 grams) was dissolved in absolute alcohol (240 cc.) containing 5.91 per cent hydrogen chloride. In the first experiment the solution was boiled during seven and three-fourths hours, in the second one during thirteen hours. The yields were 34 grams and 36.5 grams of ethylic salt, respectively. Absolute alcohol is not always readily attainable, and an attempt was made to modify the conditions so as to permit the employment of ordinary alcohol without unduly diminishing the yield of ester. The acid (45 grams) was dissolved in 90 per cent alcohol (300 cc.), concentrated sulphuric acid (20 cc.) added, and boiled in a reflux apparatus during eleven and a half hours. About one-third of the alcohol was distilled off and the residue warmed on the water-bath with sodium hydrogen carbonate until it was almost neutral and the greater portion of the remaining alcohol had volatilized; it was then poured into water, the neutralization completed with sodium hydrogen carbonate, and the ester extracted with ether. The weight of ester obtained was 42 grams, whilst 2.5 grams of camphoroxalic acid was recovered. The yield of ester, per cent of acid employed, was, in the three experiments, 75.9, 81.5, and 93.3, respectively.

Action of Aniline on Ethylic Camphoroxalate.

No reaction appears to take place when aniline and ethylic camphoroxalate, in equimolecular proportion, are boiled in a reflux apparatus with ether or benzene. A mixture of the ethylic salt with two molecular proportions of aniline, when heated at 130° during three hours, gives a good yield of phenylcamphoformeneaminecarboxylic anilide,

$$C_8H_{14}\begin{cases} C : C.CO.NH.C_6H_5 \\ | \quad\quad | \\ CO \quad NH.C_6H_5 \end{cases}.$$

The compound readily crystallizes, and is purified by repeated solution in benzene and precipitation with light petroleum; it is finally deposited in small colorless needles melting at 193°.

[1] This JOURNAL, **20**, 331 (1898).

Bromine, in chloroform solution, appears to be without action on the anilide, only a very slight diminution of the color is perceptible, and no evolution of hydrogen bromide can be detected. The compound is very stable towards alkalies, no change taking place by heating it on the water-bath, in dilute alcoholic solution, with recently precipitated lead hydroxide, during six hours, nor with sodium hydroxide during thirty minutes; prolonged boiling of the soda solution gives a similar negative result. Attempts to hydrolyze the anilide by the action of sulphuric acid have not, as yet, led to definite results; the products are usually very resinous.

I. 0.2000 gram substance gave 0.1270 gram H_2O, and 0.5618 gram CO_2.

II. 0.1927 gram substance gave 0.5420 gram CO_2.

III. 0.3058 gram substance gave 20.6 cc. nitrogen at 23°.5 and 747 mm.

IV. 0.1945 gram substance gave 13.6 cc. nitrogen at 28° and 744 mm.

V. 0.1673 gram substance gave 12 cc. nitrogen at 26°.5 and 743 mm.

	Calculated for $C_{24}H_{26}N_2O_2$.	Found.				
		I.	II.	III.	IV.	V.
C	77.00	79.60	76.70	....	....	....
H	6.95	7.05	....	....	....	....
N	7.49	....	....	7.44	7.50	7.75

Some difficulty was encountered in determining the carbon, hence, in order to avoid, if possible, the formation of graphite, analysis II. was carried out in a current of moist oxygen.

An unsuccessful attempt was made to prepare the aurochloride and platinochloride by mixing an alcoholic solution of anilidocamphoformeneaminecarboxylic anilide, containing a little hydrochloric acid, with alcoholic solutions of auric chloride and platinic chloride, respectively, and allowing the liquid to evaporate spontaneously. The gold salt was reduced and the solution deposited a dark resinous mass; from the platinum solution reddish crystals were obtained, but after purification they became colorless, melted at about 190°, and consisted of the original anilide. If formed at all, the platinochloride is evidently unstable.

Oxidation of Ethylic Camphoroxalate Phenylhydrazide.

Ethylic camphoroxalate phenylhydrazide was suspended in absolute alcohol and mixed with recently precipitated pasty anhydrous mercuric oxide, but no action took place after remaining at the ordinary temperature during ten days. Anhydrous ether was substituted for the alcohol, and the mixture boiled during seventeen hours. As only a slight darkening was perceptible, the ether was removed and benzene added, but no effect was produced by ten hours' additional boiling at the higher temperature so obtained. The oxidation takes place readily by the action of hydrogen peroxide in ethereal solution. Aqueous hydrogen peroxide (10 vols. per cent U. S. P.) is extracted three times with ether; the combined extracts, which equal the aqueous solution in volume, are dried, and added to the phenylhydrazide ground to a paste with ether. The hydrazide quickly dissolves, and the solution is allowed to remain over night at the ordinary temperature. After removing the ether a red crystalline residue is obtained which is recrystallized from benzene. From this solvent apparently two kinds of crystals are deposited, hexagonal plates, and tufts of needles. Fractional recrystallization from ethylic acetate, with the addition of light petroleum, gives, by spontaneous evaporation, red needles, which, when crushed, form a white powder and melt at 210°.

0.2973 gram substance gave 22.7 cc. nitrogen at 23°.5 at 746 mm.

	Calculated for $C_8H_{14}\langle^{C:C.CO.OC_2H_5}_{CO\ N:N.C_6H_5}$.	Found.
N	8.23	8.42

The compound is only slowly attacked by glacial acetic acid, in which respect it differs from the original hydrazide.

The less soluble fraction of the oxidation-product, after further purification, melted at 108°–109°. It was obtained only in very small quantity, and could not be completely freed from traces of hydrazide. It is probably identical with the compound (m. p. 112°) described by Bishop Tingle in a previous paper.[1]

[1] *Loc. cit.*

Action of Isoamylic Alcohol on Camphoroxalic Acid.

Camphoroxalic acid (44.8 grams) was dissolved in isoamylic alcohol (240 cc.) containing hydrogen chloride (10.99 grams = 4.57 per cent), and boiled during nine hours. The greater portion of the alcohol was then distilled off, and the residue washed with sodium hydrogen carbonate solution, which removed 3.7 grams camphoroxalic acid. The product could not be induced to crystallize. Since it evidently contained isoamylic alcohol it was heated during a considerable time on the water-bath, at first in an open vessel and finally in a current of dry air under reduced pressure. It failed to give crystals by this treatment, so a portion was distilled under a pressure of 25 mm.; some alcohol passed over, but above 95° decomposition commenced, and the same result took place when another portion was distilled in steam. When hydrolyzed, camphoroxalic acid was quantitatively regenerated from the crude substance.

Preparation of Ethylic Pyrotartrate.

Pyrotartaric acid (25 grams) was dissolved in absolute alcohol (100 cc.) containing hydrogen chloride (3.38 grams), and the solution boiled during four and a half hours. The alcohol was distilled off on the water-bath, the residue dissolved in ether, and washed with a solution of sodium hydrogen carbonate. The ethereal solution was then dried and the ether removed. The yield of ester was about 80 per cent of the theoretical. Sulphuric acid may be substituted for the hydrogen chloride with equally good results.

Action of Ethylic Pyrotartrate on Camphor.

For the reasons detailed in the theoretical portion of this paper we commenced a study of the interaction of ethylic pyrotartrate and camphor in presence of sodium and of sodium ethoxide. Ethylic pyrotartrate (28.7 grams) and camphor (34.5 grams) were dissolved in light petroleum (250 cc.), and sodium wire (3.5 grams) added. A slow action took place, but heating on the water-bath during three hours was required to bring it to completion. The product, after standing

over night, was poured into water and the petroleum removed, giving solution *A*. The aqueous liquid was extracted with ether, giving solution *B*. It was then acidified with dilute sulphuric acid and again extracted several times with ether, giving solution *C*. After removal of the solvents the residues *A* and *B* were united and warmed with aqueous potash. Apart from borneol and camphor, the only definite product that could be obtained was pyrotartaric acid. Solution *C* yielded an oily residue, which gave a red coloration with alcohol and ferric chloride, showing that a condensation-product of ethylic pyrotartrate and camphor had been produced. The compound is comparatively unstable towards alkali, since, when heated with dilute sodium hydrate, it is converted into its constituents. In a second experiment the mixture of ethylic pyrotartrate, camphor, sodium wire, and light petroleum, in the same proportions as before, were boiled during ten minutes, and then absolute alcohol (10 cc.) was added through the reflux apparatus. The subsequent treatment was similar to that described above, and gave essentially the same result, as did also an experiment in which a dilute, absolute alcoholic solution of sodium ethoxide was employed in place of the sodium wire and light petroleum. The investigation will be resumed at the first opportunity.

Action of Ethylic Oxalacetate on Camphor.

Ethylic oxalacetate (18.8 grams) and camphor (22.8 grams) were dissolved in light petroleum (250 cc.), and sodium wire (2.3 grams) added. A reaction readily took place, and was completed by gently warming on the water-bath. The product was treated in the manner described above in the first experiment with camphor and ethylic pyrotartrate. On acidifying the aqueous solution, after the removal of the borneol, etc., the liquid acquired a blue-purple color, which disappeared on agitation with ether, the latter becoming yellow. The residue from the ethereal solution was oily, and an attempt was made to hydrolyze it by warming it with aqueous alcoholic potash. This produced a dark-red solution. The heating was continued until a drop of the alkaline liquid com-

pletely dissolved in a large volume of water. It was then acidified and extracted with ether. After removal of the ether, the residue was again oily, and could not be induced to crystallize. The compound has well-defined acidic properties and liberates carbonic anhydride from a solution of sodium carbonate. With hydrochloric acid in slight excess the blue color is produced as described above, but it disappears on the addition of a larger proportion of acid. When the compound is heated under reduced pressure (50 mm.) an evolution of gas commences below 95°. The barium salt is colorless and sparingly soluble, but attempts to purify the acid by means of it did not lead to definite results. The borneol extract, formed during the preparation of the above compound, was examined for an acid corresponding to camphoroxalic acid, but without success. The probable nature of the compound is discussed in the theoretical portion of this paper.

Action of Ethylic Oxalate on Thymol.

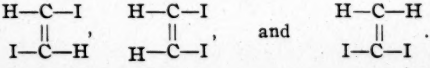
Ethylic oxalate reacts with thymol in solution in light petroleum, in presence of sodium wire. The product has hitherto been obtained only as an oil and appears to be somewhat unstable. It gives a dark-red coloration with alcohol and ferric chloride. We have also obtained some evidence of the production of a compound corresponding to camphoroxalic acid, but have not hitherto succeeded in isolating it from the admixed borneol and camphor. We are continuing this research in various directions.

LEWIS INSTITUTE, CHICAGO, ILL.

ON A LIQUID ACETYLENE DIIODIDE.

BY EDWARD H. KEISER.

According to our present theories of the constitution of organic compounds two symmetrical and one unsymmetrical acetylene diiodide are possible. The constitution of these is represented by the following formulas:



The first and second represent stereoisomers, the former being the fumaric, the latter the maleic form.

Up to the present time but one acetylene diiodide has been obtained with certainty. This is the well-known solid crystalline compound melting at 73° and boiling at 192°, which is obtained by conducting a current of acetylene through a solution of iodine in alcohol or in potassium iodide.

A liquid acetylene diiodide is mentioned by Sabanejeff,[1] who prepared the crystalline diiodide from acetylene and an alcoholic solution of iodine, and found that the alcoholic solution from which the solid diiodide had separated gave, on the addition of water, an oily liquid. This liquid, when cooled down, solidified. A few degrees above 0° it again partially liquefied. The liquid part was poured off from the solid (the latter was found to be the crystalline diiodide) and again cooled down and solidified. On warming, the portion which first melted was again poured off, and this process of freezing and melting was repeated several times until no more solid diiodide could be removed from the liquid substance. An analysis of this liquid indicated that it had the same percentage composition as the solid acetylene diiodide, and its empirical formula was found to be $C_2H_2I_2$.

Sabanejeff apparently obtained but small quantities of this liquid since he was unable to characterize the compound sharply. He states that at a few degrees below 0° it becomes solid, its specific gravity is 2.942 at 21°, and that it decomposes on distillation.

In 1889 Paterno and Peratoner,[2] in studying the action of acetylene upon iodine in alcoholic and acetic acid solution, were unable to obtain the liquid diiodide of Sabanejeff. The oily liquid which separates on adding water to the alcoholic mother-liquor from which the crystalline diiodide has been removed is not, according to Paterno and Peratoner, a definite compound but a mixture. They also obtain the oil by acting upon a solution of iodine in glacial acetic acid with acetylene. One-fifth of the weight of the oil is solid diiodide, the remainder consists of a liquid, which is found by analysis and molec-

[1] Ann. Chem. (Liebig), 178, 120. [2] Gaz. Chim. Ital., 19, 1889; and 20, 670.

ular weight determination to have the formula $C_4H_4I_2O_2$. They studied the behavior of this liquid compound with phosphorus pentachloride and obtained acetyl chloride. Treated with sodium amalgam, it gave acetic acid; oxidation with chromic acid likewise gave acetic acid. From these facts they conclude that the constitution of the compound is to be represented thus: $CH_3COO—CI=CHI$.[1]

Action of Acetylene upon Iodine.

In attempting to prepare the solid acetylene diiodide by the direct action of acetylene upon iodine, without the intervention of a solvent, 10 grams of iodine crystals were put into a 500 cc. flask and the air in the flask was displaced by acetylene. The gas was prepared from calcium carbide, and was purified by passing it through a series of wash-bottles containing nitric acid, alkaline lead solution, concentrated caustic potash, and copper sulphate in the order mentioned. The acetylene then was dried with calcium chloride before entering the flask.

Acetylene is apparently without action upon iodine in the cold. On warming the flask so that the iodine melts and the interior is filled with the violet vapor, a slow absorption of the gas begins. Instead of heating the flask with a free flame, as was done in the earlier experiments, it was found preferable to suspend it in a paraffin bath, and to keep the temperature of the bath at from 140°–160°. Under these conditions a slow but regular absorption of acetylene takes place, and after from twenty-four to thirty-six hours the color of the iodine will have disappeared. When cold, the flask contains a mass of crystals, but also an amber-colored liquid, which can readily be poured off from the crystals. The yield of liquid appeared to be greater if the temperature of the bath was kept at from 150°–160° than if the temperature was 120°–130°.

The crystals obtained in this way are the ordinary well-known solid acetylene diiodide. They melt at 73°. The liquid that is poured off from the crystals is saturated with the solid diiodide, and on cooling it down to 0° a further quantity of the crystals separate. On cooling the liquid to

[1] Beilstein: Organ. Chemie, I, 196.

—23° it completely solidified. On warming gently and pouring off the portion which first melted, then freezing this part again, partially melting and pouring off the liquid, and repeating this process three or four times, a liquid was obtained which had a constant boiling-point, *viz.*, 185°, and which solidified at —21°.

Another method of separating the liquid from the crystalline diiodide depends upon the difference in solubility of the two substances in 50 per cent alcohol. The liquid compound is somewhat soluble in alcohol of this strength; the solid is practically insoluble. If then the liquid compound containing some of the solid diiodide in solution is shaken up with 50 per cent alcohol, the liquid dissolves, and the solid remains behind. On pouring off the alcoholic solution and adding water, the liquid compound is precipitated and separates as a heavy oil.

The pure liquid compound thus obtained is clear and colorless; in diffused daylight it slowly turns violet in color; the same change takes place rapidly in the sunlight. It is insoluble in water, readily soluble in alcohol and organic solvents. It boils at 185° (uncorr.) and solidifies at —21°. It is readily volatile with steam. Its specific gravity at 20° is 3.0625. It gives no precipitate with ammoniacal cuprous chloride.

The following results were obtained on analysis:

0.2561 gram substance gave 0.0785 gram CO_2, and 0.0166 gram H_2O.

0.2389 gram substance gave 0.3931 gram AgI, and 0.0030 gram metallic Ag (Carius' method).

These results indicate that the formula of the compound is $C_2H_2I_2$.

		Calculated.	Found.
C_2	24.0	8.58	8.36
H_2	2.0	0.715	0.72
I_2	253.7	90.705	90.37
	279.7	100.000	

The vapor of this liquid acetylene diiodide can be heated to

230° without decomposition, and a determination of the molecular weight of the compound was made by the vapor-density method of Victor Meyer. Thymol was used as the heating fluid, boiling at 230°.

0.0749 gram substance gave 6.2 cc. air at 19° and 753 mm. pressure. D = 10.3.

	Calculated.	Found.
Molecular weight $C_2H_2I_2$	280	296

An interesting fact noticed in regard to this liquid acetylene diiodide is that when it is allowed to stand in contact with aqueous hydriodic acid it is slowly changed into a mass of crystals. This change takes place more rapidly if the acid is warmed on the water-bath. These crystals melt at 71°, and an examination shows that they are the ordinary solid diiodide.

With zinc dust the alcoholic solution of the liquid diiodide evolves acetylene.

From these facts the conclusion seems justified that this new liquid acetylene diiodide is a stereoisomer of the solid diiodide, and stands in the same relation to the solid diiodide that maleic acid does to fumaric acid. The following space-formulas represent this relationship:

Solid acetylene diiodide, m. p. 73°.

Liquid acetylene diiodide, b. p. 185°.

That the liquid diiodide should have the unsymmetrical formula $H_2C{=}CI_2$ seems very improbable on account of the behavior of the substance as described above and also on account of its great stability in the air. Aside from the slight color change produced by light it seems to be entirely unaffected by air. The unsymmetrical chloride and bromide, $CH_2{=}CCl_2$ and $CH_2{=}CBr_2$, are very unstable substances. They readily undergo polymerization, and they absorb oxygen from the air, forming acetyl derivatives.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
January, 1899.

A SIMPLE COLOR REACTION FOR METHYL ALCOHOL.

By S. P. Mulliken and H. Scudder.

In view of the importance of methyl alcohol to the chemist, and its frequent formation in organic reactions, it is surprising that there should be any lack of convenient and simple tests for its identification. Some such tests have been devised for the detection of wood spirit, but they are acetone and not methyl alcohol reactions. At the present time only two direct tests for methyl alcohol are generally recommended by authorities on organic analysis, and of these neither is of such a character as to be extensively and freely used in the every-day practice of the laboratory.

One of these methods, due to Rich and Bardy,[1] depends on the successive conversion of methyl alcohol into methyl iodide, dimethylaniline, and methylaniline violet, by a series of complicated operations that require about twelve hours for their performance. By this method, which, were it not for its tedious length, would have much to commend it to the analyst, one part of methyl alcohol may be detected with certainty in the presence of more than 100 parts of ethyl alcohol.

The second test alluded to, that of J. T. Miller,[2] depends on the oxidation of methyl alcohol to formic acid by means of a mixture of potassium dichromate and sulphuric acid, and the subsequent detection of the formic acid, after distillation, by its reducing action on a hot solution of silver nitrate. This test can be made in about half an hour, and is not seriously interfered with by the presence of relatively large quantities of ethyl alcohol. Its conclusiveness is, however, impaired by the fact that many soluble and volatile compounds besides methyl alcohol, *e. g.*, acetone and allyl alcohol, are also oxidized to formic acid under the prescribed conditions.

The simple test-tube reaction, whose description follows, can be directly applied to the aqueous solution of any organic distillate of low boiling-point, and completed in less than five

[1] Compt. rend., 80, 1076. [2] Allen's Organic Analysis, 3rd Edition, 1, 81.

minutes. Like all tests of its class, it has limitations that it is important to recognize; but its results are certainly less liable to misinterpretation than those of the much-used Lieben reaction for ethyl alcohol, which it excels in delicacy.

A piece of rather light copper wire is wound around a lead pencil, so as to form on one end a close spiral about 2 cm. in length. The spiral is then superficially oxidized in the upper flame of a Bunsen burner, and while still at a bright red heat, plunged into 3 cc. of the alcoholic solution contained in a test-tube. This treatment oxidizes a portion of the methyl alcohol to formic aldehyde. A second dip with the oxidized spiral is usually advisable, and in dealing with solutions containing less than 0.1 per cent. of methyl alcohol, as many as three or four additional dips, the tube being cooled each time with tap water. This method of oxidation has the important advantage over others tried, that it does not go too far, and does not give troublesome by-products. *A concentrated spirit should always be diluted with at least three or four volumes of water before oxidation.*

One drop of a 0.5 per cent aqueous solution of resorcin is next added to the weak solution of formic aldehyde, and the mixture very cautiously poured down the side of an inclined test-tube containing a few centimeters of concentrated sulphuric acid. The presence of methyl alcohol is indicated by the appearance of a pure rose-red zone at the line of demarcation between the denser and lighter layers. In and above this very characteristic band of color is suspended a scanty white or pinkish coagulum, which, after long standing, increases notably in color intensity, and finally separates and rises in purplish-red flocks.

In testing for traces of methyl alcohol, the use of a large excess of resorcin is to be carefully avoided. Too much of this reagent tends to destroy the purity of the rose color besides rendering the test less delicate. Thus, while 1 drop of a 0.5 per cent solution of resorcin is the best quantity for use in testing solutions containing 0.1 per cent of methyl alcohol, 0.01 of a per cent of methyl alcohol can be recognized only when the quantity of resorcin is reduced to one-tenth of

that employed in the first instance, and the mixture then allowed to stand for an hour or more.

It is to be remembered that the more common methyl esters and ethers are all slightly hydrolyzed when dissolved in water. Such solutions, since they contain free methyl alcohol, also give this reaction. The only other compounds examined by us, which, when tested in the manner just described, give colorations in the least resembling that caused by methyl alcohol, are secondary and tertiary butyl alcohols, dimethylethylcarbinol, and formic acid. In the case of these rare secondary and tertiary alcohols, the pink zone is separated from the acid by a lower band of lemon-yellow, and the red coloring-matter does not separate and rise to the surface in solid flakes. The coloration from formic acid is so faint as to be scarcely noticeable, even when the solution tested contains as much as 5 per cent of the acid. To preclude the possibility of mistakes arising from the presence of formic acid, mixtures that react strongly acid should be neutralized by the addition of a little sodium carbonate before distillation.

Most primary alcohols are oxidized by the hot copper spiral to aldehydes, and these aldehydes, on treatment with sulphuric acid and resorcin, then yield oxyfluorones or other more or less colored condensation-products of undetermined composition. Fortunately, so far as our experiments enable us to judge, none of the colors produced in this way needs be mistaken for that given by methyl alcohol. Ethyl, propyl, isopropyl, butyl, isobutyl, amyl, hexyl, octyl, capryl, and allyl alcohols, as also ethyl ether, acetone, furfurol, lactic acid, and the carbohydrates, arabinose, dextrose, lævulose, sucrose, maltose, and lactose, all give shades of yellow, amber or ocherous-brown.[1] The polyatomic alcohols like glycerin and erythrite give brownish-purples. Chloroform and many other non-oxygenated bodies give no coloration whatever. We desire particularly to emphasize the failure of the carbohydrates to give red colorations with sulphuric acid and

[1] The investigations of Mylius and of v. Udranszky (Zeit. f. physiolog. Chem., 11, 492; 12, 355 and 377), show that the brownish colorations given by the carbohydrates must be attributed to a reaction between resorcin and furfurol. The latter compound is always present among the products of the decomposition of carbohydrates by sulphuric acid.

resorcin, because certain remarks made during the discussion of this paper, when read before the Chemical Section of the American Association for the Advancement of Science, last August, left the entirely erroneous impression on the minds of many who were present, that the same red coloration would be produced by the carbohydrates under these circumstances, as is shown in the Fischer and Jennings reaction,[1] in which the glucoside condensation-products yielded by carbohydrates and resorcin under the influence of hydrochloric acid are oxidized in alkaline solution by Fehling's reagent.

In dealing with mixtures which contain color-producing organic constituents not removable by neutralization and distillation, it is also a fortunate circumstance that the rose color due to formic aldehyde usually tends to make its appearance in a state of greater or less purity in a narrow band next to the acid, while the other color forms a wider zone just above and shading into the first. When the substances that give the yellow or brown color are present in large excess, the delicacy and certainty of the reaction may be seriously impaired or destroyed. One part of methyl alcohol may, however, be detected without great difficulty in the presence of five, and after a little practice, though with less certainty, in as many as ten parts of ethyl alcohol.

Several color reactions between formic aldehyde and phenols have been recommended at different times for diagnostic purposes, but we find no evidence on record that the colored substances formed in these tests have ever been isolated or identified. Möhlau and Koch have, however, shown[2] that resorcin and formic aldehyde are easily condensed by sulphuric acid to methylenediresorcin; while Caro,[3] from the closely related methylenediphenol and methylenedisalicylic acid, by the use of sulphuric acid and an oxidizing agent, has synthesized the red colors aurin and aurintricarbonic acid. Now since either phenol or salicylic acid, when substituted for resorcin in the test for formic aldehyde, give rose-colored bands and flakes scarcely distinguishable in hue from those pro-

[1] Ber. d. chem.Ges., **27**, 1350. [2] *Ibid.*, **27**, 2887.
[3] *Ibid.*, **25**, 941 and 948.

duced by the use of resorcin, one might naturally suspect that the color from resorcin would be resaurin:

$$CH_2.[C_6H_3(OH)_2]_2 + C_6H_4(OH)_2 + O_2 =$$

Methylenediresorcin.

$$[(OH)_2C_6H_3]_2.C\begin{cases} O \\ \cdot \\ C_6H_3OH \end{cases} + 2H_2O.$$

Resaurin.

Upon studying the action of solvents on the red flakes, this explanation at first seemed discredited. Resaurin is readily soluble in dilute alkalies or in hot alcohol. But the flakes from a methyl alcohol test may be boiled with alcohol for a long time without losing any appreciable portion of their color, which is only darkened, but not dissolved out when treated with alkalies. On the other hand, if formic aldehyde and resorcin in rather concentrated solutions are mixed in the proper proportions, and poured upon strong sulphuric acid, a body is obtained which shows all the properties and reactions of resaurin,—the same behavior with alkalies, acids, and reducing agents, and the characteristic resaurin absorption spectrum. Our study of this question is not concluded, but the indications are, that if the color observed in the test is not caused by a very little resaurin entangled and protected by a great mass of insoluble, colorless condensation-products, it is at least a body chemically related to resaurin—perhaps a diphenylmethane color.

Hehner[1] seems to have been the first to suggest the detection of formic aldehyde by its zone reactions with phenols and sulphuric acid. For this purpose he particularly recommends the employment of carbolic acid. According to our experience, phenol gives a less intense color than resorcin. Hehner also recommends milk or a solution of casein as a substitute for phenol; but casein is not a suitable reagent for the methyl alcohol tests, because the oxidation-products of ethyl alcohol yield with it the same blue color as formic aldehyde; though singularly enough solutions of pure acetic aldehyde did not give us this result.

[1] Analyst, **21**, 20; **20**, 155.

Lebbin's reaction,[1] which depends on the appearance of a strong red color when formic aldehyde is boiled with a solution of resorcin and caustic soda, gives satisfactory results when applied to aqueous solutions of pure methyl alcohol that have been treated with a hot oxidized copper spiral; but if even small quantities of ethyl alcohol are present it fails completely.

Trillat's reaction between formic aldehydes and dimethylaniline, gives a strong, pure blue color. A solution containing 1 per cent of methyl alcohol and 10 of ethyl alcohol, still gives a blue of admirable purity, while in the presence of even twice this quantity of ethyl alcohol the result is seldom doubtful. The proper execution of the test requires nearly an hour. This is its chief disadvantage. It is occasionally very serviceable as a confirmatory reaction in the examination of mixtures containing so much ethyl alcohol that the test with resorcin, while pointing to the probable presence of methyl alcohol, is not quite conclusive.[3]

MASS. INSTITUTE OF TECHNOLOGY,
December 7, 1898.

REACTIONS FOR THE DETECTION OF THE NITRO-GROUP.

BY S. P. MULLIKEN AND E. R. BARKER.

There are few radicals of equal importance whose detection in organic compounds by direct qualitative tests is so inadequately provided for as is that of the nitro-group. Vortmann, in his "Anleitung zur chemischen Analyse organischer Stoffe," enumerates only three reactions designed for this purpose; *viz.*, reduction to the amido-group, formation of chlorpicrin, which may be recognized by its odor when a nitro-compound is boiled with a solution of bleaching-powder,

[1] Ztschr. anal. Chem., 1897, 518. [2] Compt. rend., **116**, 891.

[3] In the current (December) number of the Bulletin de la Société chimique de Paris and in a preliminary article in the Comptes rendus, **19**, 235, Trillat has recently published an interesting method for the detection and estimation of methyl alcohol, which, both on account of its intrinsic importance, and of its bearing on the resorcin test, would have received due attention in the present paper, had the authors known of Trillat's work at the time when their manuscript was prepared for publication.

and the reddish or yellowish colorations produced by boiling solutions of alkaline hydroxides.

According to Vortmann all nitro-compounds give the chlorpicrin reaction. This is evidently a mistake, for with the exception of the nitrophenols aromatic nitro-bodies almost never yield appreciable quantities of chlorpicrin. The color reaction with caustic potash is lacking in precision and is never conclusive. It is therefore nearly always necessary to base the identification of the nitro-group on the results of the reduction test and on physical properties. This procedure would be fairly satisfactory, if the products from such reductions only agreed in presenting some one common property or reaction so striking as to be readily recognized. But instead of meeting with uniformity in the appearance and properties of such reduction-products, we find ourselves confronted by phenomena of the greatest diversity; for an amido-compound may be either a liquid or a solid, colored or colorless, fragrant or odorless; it is often a strong base, but it may exhibit none of the more familiar basic properties and reactions. In short, after the reduction has been properly performed, very skilful and critical interpretation of the experimental data may be demanded to prevent the possibility of deception.

The object of this paper is to call attention to two additional qualitative reactions for the nitro-group, which, while seldom seriously interfered with by the presence of other radicals, possess a distinct advantage over the older tests in the singularly clear-cut and definite character of their visible phenomena.

The first of these tests depends on the fact that all nitro-compounds when dissolved in dilute alcohol containing traces of some neutral salt like calcium chloride are very easily reduced to zinc dust by hydroxylamines. This method for obtaining hydroxylamines was first used nearly simultaneously in 1895 by E. Bamberger[1] and by A. Wohl[2] for the preparation of phenylhydroxylamine. The use of calcium chloride as an accelerating agent is due to Wohl. Three years previous to the work of Bamberger and Wohl, V. Meyer[3] had

[1] Ber. d. chem. Ges., **27**, 1347. [2] *Ibid*, **27**, 1434.
[3] *Ibid*., **24**, 3528.

prepared various aliphatic hydroxylamines by reducing fatty nitro-bodies with zinc and hydrochloric acid; but his method is not applicable in the aromatic series. As a qualitative test this reaction is best applied by dissolving 3 or 4 drops of the nitro-body under examination in 3 cc. of 50 per cent alcohol, adding 5 or 6 drops of a 10 per cent solution of calcium chloride, and then heating until violent boiling begins. Chemical action accompanied by frothing will continue for some time without further application of heat. In dealing with unknown compounds it is advisable to allow the mixture to stand from two to five minutes before filtering, although so much time is seldom absolutely necessary. The presence of a hydroxylamine derivative in the filtrate from the reaction may easily be shown by pouring a few drops of the clear liquid into some strongly ammoniacal solution of silver nitrate in dilute alcohol. The hydroxylamines are all powerful reducing agents and we have never met with any nitro-body, which, when treated in the manner just described, does not yield enough hydroxylamine to give either a silver precipitate or a mirror. A white or light yellow precipitate is without significance.

In the aliphatic series this test has been tried successfully with mononitro-derivatives of methane, ethane, and pentane, and with chlorpicrin; in the aromatic series with mononitro-derivatives of benzene, toluene, naphthalene, chlorbenzene, brombenzene, anisol, cinnamic acid dibromide, benzoic acid, benzenesulphonic acid, and with *p*-nitrophenylpropiolic acid; with dinitro-compounds of benzene, aniline, and phenol; and with trinitro-derivatives of benzene, toluene, xylene, phenol, and triphenylmethane. The only important classes of nitrogenous carbon compounds not containing the nitro-radical, which, while unable to reduce ammoniacal silver nitrate solution in the cold, were found to gain the power to do so after the treatment with zinc dust, are nitroso, azo, and azoxy bodies. The reduction-products from bodies of the first class are hydroxylamines or hydrazines, while those from the second and third are hydrazo-compounds.

The principle involved in the second reaction for the nitro-group is borrowed from the well-known Coupier process for

the manufacture of magenta. In this process nitrobenzene, in the presence of a little iron and hydrochloric acid, acts as an oxidizing agent in the conversion of "aniline-red oil" into rosaniline. Lange, in studying the mechanism of Coupier's method,[1] demonstrated that nitrobenzene is not necessary to insure the production of pure rosaniline, but that chlornitrobenzene, nitrotoluene, and certain other substituted derivatives may be used to replace it without causing any change in the chemical composition of the dye-stuff resulting, from which he reasoned that the nitro-compound in all such cases furnishes nothing directly to the structure of the rosaniline molecule, but that it simply provides oxygen for the oxidation of the aniline bases. Nitrosobenzene, methylphenylnitrosamine, azo-, azoamido-, and hydrazobenzene, Bismarck brown and helianthine may be mentioned as examples of bodies found to show this behavior.

After numerous experiments, the following procedure was finally adopted as affording the most convenient means for applying Coupier's principle in the form of a simple qualitative test. Three or four drops of the nitro-compound are boiled for two or three minutes in a test-tube with 2 cc. of "aniline-red oil" (made by mixing equal parts of aniline, *o*-toluidine and *p*-toluidine), 2 cc. of distilled water, 2 cc. of concentrated hydrochloric acid (sp. gr. 1.20), and about 1 gram of iron filings. The liquid reagents should be carefully measured from a small graduate, a large excess of acid entirely preventing the appearance of a color, while too little diminishes its intensity and purity. The red color of the rosaniline is best observed by pouring a few drops of the dark-colored liquid produced in the experiment into a test-tube half-filled with dilute acetic acid. A blank test performed in the same manner, except that the nitro-compound is omitted, gives no color, or at most a pale yellow.

The "aniline-red oil" used as a reagent, if not nearly colorless to begin with, should be made so by distillation. It will then remain in good condition several months, if preserved in a closely-stoppered bottle of dark glass.

[1] Ber. d. chem. Ges., **18**, 1918.

The rosaniline reaction has been experimentally verified for all the nitro-compounds included in the list given in connection with the description of the silver reduction test, excepting only nitromethane, nitroethane, and chlorpicrin, which are so volatile as to boil off before oxidation can begin; and the trinitro-compounds, which give dirty reddish or greenish-browns. The color from dinitro-compounds is redder than that given by trinitro-bodies, but it is very far from having the strength or purity of that obtained from substances containing only a single nitro-group.

Upon extending our experiments to compounds not containing the nitro-group, it was soon found possible to lay down the rule, that the appearance of a red color may be generally anticipated whenever an organic body containing oxygen directly linked to nitrogen is subjected to the treatment with aniline bases. Azoxybenzene, nitrosobenzene, methylphenylnitrosamine, acetoxime, and ethyl nitrate and nitrite furnish good illustrations of the truth of this statement. Iodosobenzene and iodobenzene also give purplish-red solutions, which may perhaps contain fuchsin. Of the two well-known organic oxidizing agents, chloranil and quinone, the first gives only a dirty yellow, and the second a coffee-brown. Other classes of organic compounds, so far as is known, yield no decided colors.

Inorganic oxidizing agents, such as nitrates and nitrites, arsenic acid and mercuric chloride, do not usually give pronounced colorations; but since slight changes in the experimental conditions might lead to the formation of fuchsin, the absence of such substances should be established before giving full weight to the conclusions drawn from any experiment.

After what has been already stated, no detailed comparison of the merits of the three chief tests for the nitro-group will be necessary. As generic reactions, the two new tests, if employed together, will be found to be more uniformly reliable and convenient in practice than the older method of reduction with tin and hydrochloric acid; while on the contrary, the acid reduction process may evidently be made to supply more new and useful data when the problem in hand is to complete

the identification of some particular nitro-compound. None of these methods can furnish absolute proof of the presence of the nitro-radical; but the maximum of certainty attainable by their use alone is reached by the simultaneous employment of the fuchsin with one of the reduction tests—a combination which when a positive result is obtained eliminates the possibility of mistakes that might occur in consequence of the reduction of azo-groupings.

MASS. INSTITUTE TECHNOLOGY,
December 24, 1898.

REVIEWS.

KURZE ANLEITUNG ZUR QUALITATIVEN ANALYSE (EINLEITUNG IN DIE CHEMISCHE ANALYSE; ERSTES HEFT). VON DR. LUDWIG MEDICUS. 8te u. 9te Auflage. Tübingen. H. Laupp. 1898. viii + 158 pp.

Intended as an introduction to the study of chemical analysis in its technical applications, this little book gives, without any preliminary instruction in manipulation, an orderly account of the reactions usually employed for the detection of the more common basic and acid radicals in inorganic compounds, then a rather condensed scheme for the separation of these, an exceedingly brief notice of the rarer elements, with indications of their behavior with the principal group reagents, and at the end a few individual examples for practice. The work is evidently adapted for use, as a kind of syllabus, in laboratory teaching of beginners, and has scarcely anything to distinguish it from the multitude of such little manuals in sundry languages. J. W. M.

THE PRACTICAL COMPOUNDING OF OILS, TALLOW, AND GREASE, FOR LUBRICATION, ETC. By an Expert Oil Refiner. London: Scott, Greenwood & Co. New York: D. VanNostrand Co. Cloth, 8vo. pp. 96. Price, $3.50 net.

The scope of the book is indicated in the title. In addition a few of the rough-and-ready physical and chemical tests for some of the oils are included. It contains about 60 recipes for mixing all the various oils, from the burning fluids to the heavy cylinder lubricants. In the latter the percentage of animal or vegetable oil recommended is much more than it is customary to employ in this country.

The requirements for the various lubricants, the importance of suiting the oil to the work, the necessity of cleanliness and the general unreliability of oil dealers' data show a thorough familiarity with the subject. The viscosity of the oils is stated in comparison with water, rather than in seconds, as is customary. The use of Gray's flash tester is also unusual.

It is pleasing to note the statement that "the best all-round mineral oils come from America," and that the Russian oils are inclined to clog the machinery. The book would seem to be of great value both to the manufacturer and to the analyst; the price, however, considering its size and value, is disproportionate, if not extortionate. A. H. GILL.

LIGHTING BY ACETYLENE. GENERATORS, BURNERS, AND ELECTRIC FURNACES. By WILLIAM E. GIBBS, M.E. Second Edition, Enlarged and Revised. New York: D. Van Nostrand Co. 1898. 160 pp. Price, $1.50.

Mr. Gibbs's treatment of acetylene, and of carbide furnaces, is very brief; indeed, though this is the second edition of his book, he does not mention the Horry furnace in which all American carbide is now made, but confines his descriptions to older types. His chapter on lamps and burners is better. He gives the requirements of the New York Board of Fire Underwriters, and an incomplete list of United States patents for furnaces and carbides, and a full list of generator patents. He divides generators into three classes: In the first, water is supplied in measured quantity to an excess of carbide in closed vessels; in the second, the carbide is immersed or withdrawn from water; and in the third, measured quantities of carbide are dropped into a large excess of water. The author concurs with foreign authorities in approving the use of the third type as safer and as furnishing a better quality of acetylene. The beautiful work of Lewes on this subject was published since the first edition of this book, and the author gives an abstract of it.

Mr. Gibbs's book is good, as far as it goes, though by no means exhaustive. In fact the whole subject of acetylene is developing with such rapidity,—new processes elbowing out others scarcely a year old, new suggestions, experiments and practical applications pouring in,—that a book representing the actual state of things to-day would have to be rewritten in a few months, and it is to be regretted that Mr. Gibbs in publishing a second edition did not revise it more thoroughly. Still, as the only book on the subject in English, it will be welcome. E. R.

PHYSICAL CHEMISTRY FOR BEGINNERS. By DR. CH. VAN DEVENTER, with an introduction by PROF. J. H. VAN 'T HOFF. Authorized American Edition from the German Edition. Translated by BERTRAM B. BOLTWOOD, PH.D., Instructor in Physical Chemistry in the Sheffield Scientific School of Yale University. First edition, first thousand. New York: John Wiley & Sons; London: Chapman and Hall, Limited. pp. 154. 1899.

The German edition of Van Deventer's book having been

reviewed in this JOURNAL (Vol. 19, 916), it is only necessary to call attention to the appearance of the American edition.

Whatever may be said in reference to translating an advanced work does not apply to an elementary one. While it is generally true that any one who can read an advanced treatise on a subject can read it in the original (if this is French, German, or English) the same does not hold for elementary books. There are many students of chemistry who can read the translation of Van Deventer's work to good purpose, who would be entirely unable to comprehend it in the original.

A comparison of the translation with the original shows that Dr. Boltwood has done his work with care. H. C. J.

COMMERCIAL ORGANIC ANALYSIS. Second Edition, revised and enlarged; Vol. IV: Proteids and Albuminous Principles; Proteoïds or Albuminoïds. By ALFRED H. ALLEN. Philadelphia: P. Blakiston's Son & Co. 1898.

The present volume is something more than a treatise on analytical methods or a handbook for the detection and determination of adulterations. It includes a more or less systematic exposition of the chemistry of the proteids, their derivatives and related products; indeed, few of the larger textbooks on physiological chemistry contain a more comprehensive compilation of the more recent investigations in the domain considered. Some of the papers of the past year even have found mention, being included in part in an addendum at the end of the volume.

The arrangement of the topics has apparently been determined to a large extent by the main plan of the work, *i. e.*, the presentation of the appropriate methods of commercial analysis. Of the subject matter little is to be said in the way of unfavorable criticism. The descriptions of the best methods to be employed in analysis have occasionally not been presented with as great detail as might be desired, but references to the literature are extensively given and thus the original papers readily become available to the reader who demands more precise information.

In view of the rapid advances which the chemistry of the proteids has made in recent years, it is satisfactory to find an analytical handbook which has not failed to record the results of the later investigations. The methods for the detection and distinction of the various proteids as they occur in natural or artificial products are carefully considered; thus the zinc sulphate method of Bömer for the estimation of proteoses has been introduced, and the various methods for determining proteid nitrogen are reviewed, the very satisfactory Gunning-Kjeldahl process being appropriately treated in detail. We

fancy, however, that the distillation apparatus illustrated (p. 32) will scarcely recommend itself to analysts who are accustomed to conduct a large number of determinations with far simpler arrangements. About one-third of the volume is devoted to the chemistry and analysis of milk and milk products, a large number of useful tables and valuable data regarding milk-adulteration legislation being introduced. The extensive experience of the author renders the treatment of this subject as well as the succeeding chapter on meat and meat-products of particular interest. Allen's method for the separation of the meat bases from proteids by means of bromine—to which Dr. H. W. Wiley has recently called attention (Bulletin No. 54, U. S. Dept. Agr., 1898)—is presented at length (p. 320). The method, if confirmed by a wider experience, promises to solve some of the more difficult problems connected with the analysis of meat extracts and proteid-decomposition products. The composition and preparation of the more prominent commercial proteid food-products, which are being introduced in such large numbers at present, is briefly given.

To avoid the confusion which the older significance of the term "albuminoid" might occasion, the author has found it desirable to introduce the word "proteoïd" for the class of substances (*e. g.*; gelatin, keratin, chitin, etc.) closely resembling the proteids proper. This step is only to be commended; on the other hand, the attempt at a structural formula to represent the constitution of albumin (p. 375)—a structure based upon an obviously incorrect empirical formula of a compound of unknown constitution—seems rather absurd in a book of this character. The compound lysatine, referred to in several places (pp. 16, 370, 385), has recently been shown to be a mixture of lysin and arginin; the albumose described by Salkowski as being present in the white of egg (p. 41) has become the ovomucoid of later writers. Lastly, not all physiological chemists will be inclined to admit that elastin (here classed with the fibroïds) contains no sulphur (p. 505).

There has long been a demand for a comprehensive and progressive handbook of the type which Mr. Allen has presented in Vol. IV of his "Commercial Organic Analysis." It covers a field which very few other books have treated equally well—a fact which assures the volume an appreciable acceptance.

LAFAYETTE B. MENDEL.

COMMERCIAL ORGANIC ANALYSIS, a Treatise on the Properties, Proximate Analytical Examination and Modes of Assaying the Various Organic Chemicals and Products employed in the Arts, Manufactures, Medicine, etc., with Concise Methods for the Detection and Determination of Impurities, Adulterations and Products of Decomposition, etc. By ALFRED ALLEN, F.I.C., F.C.S., Public Analyst for the West Riding of Yorkshire and the City of Sheffield; Past President Society of Public Analysts of England, etc. Third edition, illustrated, with revisions and addenda by the author and HENRY LEFFMANN, M.A., M.D., Professor of Chemistry and Metallurgy in the Pennsylvania College of Dental Surgery and in the Wagner Free Institute of Science. Vol. II. Part I. pp. 382. Fixed Oils, Fats, Waxes, Glycerol, Nitroglycerin, and Nitroglycerin Explosives. Philadelphia: P. Blakiston's Son & Co. 1899. 382 pp. Price $3.50.

"Allen's Organic Analysis" being so widely and favorably known, it seems to the writer that the review of a new edition can be best effected by stating the changes which have been made.

It being thirteen years since the appearance of the second edition, it was necessary to rewrite the whole book, an addition of sixty-four pages having been made to the matter treated; this in many cases consists of a description of the methods of the American Association of Official Agricultural Chemists.

The later methods of oil analysis are carefully and critically discussed, as for example, Twitchell's method for the detection of rosin, the bromine thermal method, and the use of the Amagat and Jean refractometer. A useful table is given for the reduction to the standard of the specific gravity of oils taken at a different temperature.

The value of the book would have been increased were the saponification *values* as well as the *equivalents* given, the latter term not having found general acceptance. While the discussion of the technology and properties of linseed oil is very exhaustive, that of lard oil is short and incomplete, which the American user will regret. In this connection it should be borne in mind that in several cases, as would be expected, adulterants of the oils are given, which never occur in this country. A serviceable addition would seem to have been a table of the approximate relative prices of the various oils and the outline of a method for examining an unknown oil.

The chapters upon soaps, explosives, and recovered oils are admirable and contain much new material, the admiralty tests being given; in the case of the oils we note the omission of the Ordway apparatus for the determination of their liability to spontaneous combustion, an account of which was published about eight years ago. Some of the illustrations seem unnecessary, as for example, the apparatus for determining the melting-points of fats, while those of the various refractometers, the use of which is described, are omitted. A. H. GILL.